mine, 79.915, necessarily has the same ratio to silver, 107.879, as the international values 79.916 and 107.880, since the same ratio is used in both sets of calculations.

By subtracting the values for the atomic weight of bromine from the molecular weight of potassium bromide, the atomic weight of potassium was obtained. The results are recorded in column 7, Table III. The atomic weight of potassium was found to agree exactly with the accepted value of 39.096, which adds more evidence in favor of this as opposed to the higher value of 39.104 obtained by Hönigschmid and Goubeau[12] and of 39.100 obtained by C. R. Johnson.[13] The work of Richards and Stähler,[14] of Baxter and MacNevin,[15] and of Hönigschmid and Sachtleben[16] agrees with the value of 39.096.

Summary and Conclusions

1. Potassium bromate has been accurately converted to potassium bromide by thermal decomposition.

2. A precise correction has been applied for the moisture content of each portion used of the recrystallized and incompletely dried potassium bromate.

3. New values have been obtained for the molecular weight of potassium bromide and the atomic weight of silver, and from these, by application of the ratio of bromine to silver (available from the work of Baxter and Hönigschmid), new values for the atomic weights of bromine and potassium have been calculated referred to the new value for silver.

4. The experimental data may be summarized as follows: Ten determinations of the ratio $KBrO_3$: KBr give a mean value of 119.011 for the molecular weight of potassium bromide. Nine determinations of the ratio KBr : Ag, using the residue from decomposition of potassium bromate, give an average value of 1.103191 and eleven determinations of the same ratio using a fused salt obtained from the reaction of pure bromine on pure potassium oxalate give an average value of 1.103195. The atomic weight of silver obtained from this ratio is 107.879.

5. The value 107.879 for the atomic weight of silver agrees within one part in 100,000 with the present accepted value, and offers an important check on the work of Hönigschmid and Sachtleben in which the absence of moisture in the initial barium perchlorate and in the final barium chloride was assumed, but only proved indirectly.

6. The atomic weights of bromine and potassium calculated from these data and the ratio Br : Ag = 0.740786 become 79.915 and 39.096, respectively.

7. If the present international value for the atomic weight of bromine (based on Ag = 107.880) is subtracted from the new value for the molecular weight of potassium bromide, the corresponding atomic weight of potassium would be 39.095.

ANN ARBOR, MICH. RECEIVED MARCH 31, 1941

---

[12] Hönigschmid and Goubeau, *Z. anorg. allgem. Chem.*, **163**, 93 (1927); **177**, 102 (1929).

[13] C. R. Johnson, *J. Phys. Chem.*, **39**, 781 (1935).

[14] Richards and Stähler, THIS JOURNAL, **29**, 623 (1907).

[15] Baxter and MacNevin, *ibid.*, **55**, 3185 (1933).

[16] Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Catalytic Effect of Water on the Aminolysis of Ethyl Phenylacetate in *n*-Butylamine

BY PAUL K. GLASOE, L. D. SCOTT AND L. F. AUDRIETH

In a series of publications from this Laboratory it has been shown that the solvolysis of esters in ammonia[1] and in amines[2] is catalyzed markedly by the addition of ammonium and amine salts, respectively. These findings have been interpreted as possible examples of acid catalysis, since "onium" salts are known to behave as acids not only in their respective parent solvents, but also in the fused state.

In view of the fact that water might also be expected to act as an acid in solvents more protophyllic than itself, care was always taken to ensure the use of absolutely anhydrous materials. It was to have been predicted that water might also

---

[1] (a) Slobutsky and Audrieth, *Proc. Natl. Acad. Sci.*, **23**, 611 (1937); (b) Fellinger and Audrieth, THIS JOURNAL, **60**, 579 (1938); (c) Audrieth and Kleinberg, *J. Org. Chem.*, **3**, 312 (1938); (d) Balaty, Fellinger and Audrieth, *Ind. Eng. Chem.*, **31**, 280 (1939).

[2] (a) Glasoe and Audrieth, *J. Org. Chem.*, **4**, 34 (1939); (b) Glasoe, Kleinberg and Audrieth, THIS JOURNAL, **61**, 2387 (1939).

exert a catalytic effect upon reactions between an ester and an amine, due to the formation of an appreciable "onium" ion concentration by reaction with the solvent.

$$RNH_2 + H_2O \rightleftarrows RNH_2{\cdot}H^+ + OH^- \qquad (1)$$

This hypothesis has now been verified experimentally for the reaction between ethyl phenylacetate and *n*-butylamine. The rate of aminolysis increases as the water content is increased, even beyond the point where the molar ratio of water to amine is greater than 1:1.[3]

Aside from the theoretical implications of the studies summarized in the present paper, it becomes obvious that rigorous exclusion of water in ammonolytic and aminolytic reactions, where these are used for the preparation of the amides and N-substituted amides from esters, is not only unnecessary but actually detrimental. Water catalyzes solvolytic reactions of this type, though not as effectively as equimolar concentrations of the respective "onium" salts. This difference is probably due to the fact that reaction (1) above takes place from left to right only to a limited extent. The actual concentration of butylammonium (and hydroxyl) ions in the resulting solution is therefore small compared with solutions containing an equimolar quantity of some butylammonium salt. While no data are available on the conductance of water in *n*-butylamine it is highly probable that water may be looked upon as a very weak electrolyte in *n*-butylamine.

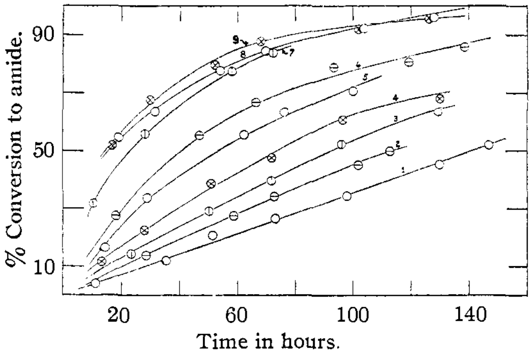

Fig. 1.—Catalytic effect of varying quantities of water on the reaction between ethyl phenylacetate and *n*-butylamine (see Table I for actual data).

Experimental

Procedure.—The procedure used in following the course of the reaction between *n*-butylamine and ethyl phenylacetate has already been described in detail in a previous publication.[2b] In the present series of experiments stock solutions were prepared in which the molar ratios of amine to ester were kept fairly constant (approximately 1.9:1) for all runs, whereas the water content was varied from 0 to 2.56 moles per mole of amine.

Discussion of Results

The reaction velocity constants (see Table I) were calculated on the assumption that the reaction between the ester and the amine is a second order reaction. This was verified by a plot of the function log $(a-x)/(b-x)$ against time. The experimental results are depicted graphically in Fig. 1 in which the percentage conversions of ester into amide are plotted against time for a series of runs in which the water content was varied systematically. The experimentally determined half-times, corresponding to 50% conversion of ester into amide, agree satisfactorily with those calculated from the specific reaction rate constants.

TABLE I

EFFECT OF WATER ON THE REACTION BETWEEN ETHYL PHENYLACETATE AND *n*-BUTYLAMINE AT 25°

a is concentration of amine in moles per liter; *b* = concentration of ester in moles per liter.

Curve no. (see Fig. 1)	Moles H_2O per liter	*a*	*b*	$K \times 10^3$	$t^1/_2$ (calcd.)	$t^1/_2$ (exptl.)
1	....	5.49	2.81	0.95	156	141
2	0.2	5.40	2.81	1.33	113	114
3	0.5	5.44	2.79	1.51	99	94
4	1.0	5.43	2.76	2.06	72	72
5	2.0	5.17	2.81	3.22	49	54
6	2.8	5.07	2.67	4.22	39	41
7	5.6	5.00	2.53	7.1	23	23
8	8.4	4.57	2.38	8.25	22	18
9	11.2	4.36	2.24	10.4	18	16

The marked dependence of the reaction rate upon the concentration of water is readily apparent from an examination of Fig. 2 in which the experimentally determined half-times (see Table I) for the various experimental series are plotted against the molar concentrations of added water. It should be pointed out, however, that a comparison of this sort is only semi-quantitative since the nature of the solutions changes not only as the water content is increased, but also during the

---

(3) It becomes somewhat difficult to speak of this effect as "acid" catalysis, especially where the mole ratios of water to amine are greater than 1:1, despite the fact that all of the work undertaken by Shatenshtein and his co-workers [THIS JOURNAL, **59**, 432 (1937)] and by investigators in this Laboratory was based upon the fact that "onium" salts should be, and actually do behave as, acids in their respective parent solvents. On the basis of unpublished work by the authors it now appears that neutral salts also catalyze solvolytic reactions between esters and ammonia, as well as amines. These catalytic effects may therefore represent examples of "electrolyte" catalysis, even though some of these electrolytes may be regarded formally as acids.

course of a single series of experiments as more and more of the ester reacts with the amine with formation of the N-substituted amide.

The catalytic effect of water upon the aminolysis of ethyl phenylacetate is not nearly as marked as that observed in the case of a number of butylammonium salts.[2b] The half-times for solutions containing 0.1 mole per liter of various butylammonium salts, with the concentrations of amine and ester approximately the same as those given in Table I, are reproduced here for comparison:

Salt	$BuNH_3Cl$	$BuNH_3SCN$	$BuNH_3ClO_4$
Half-time, hr.	33	53	70

Using 0.2 mole per liter of water, 50% conversion required 114 hours (see Table I).

There was, of course, the possibility that hydrolysis of the ester might occur in those solutions containing an appreciable quantity of water. The usefulness of this method as a preparative procedure was therefore investigated. In a typical experiment a solution containing 14.6 g. (0.2 mole) of butylamine, 16.4 g. (0.1 mole) of ethyl phenylacetate and 3.6 g. (0.2 mole) of water was allowed to stand at room temperature for four days. The reaction mixture was then poured into a dilute solution of sulfamic acid to remove excess amine, causing the separation of an oily layer of impure amide which solidified on cooling. This product was filtered, dried and recrystallized from high boiling petroleum ether, yielding 16 g. of the purified N-*n*-butylamide of phenylacetic acid (84% of the theoretical yield). The compound melts at 57° and is soluble in ethanol, ether and chloroform, but insoluble in water.

Anal. Calcd. for $C_6H_5CH_2CONHC_4H_9$: N, 7.36; H, 8.9; C, 75.3. Found: N, 7.1; H, 8.8; C, 75.1.

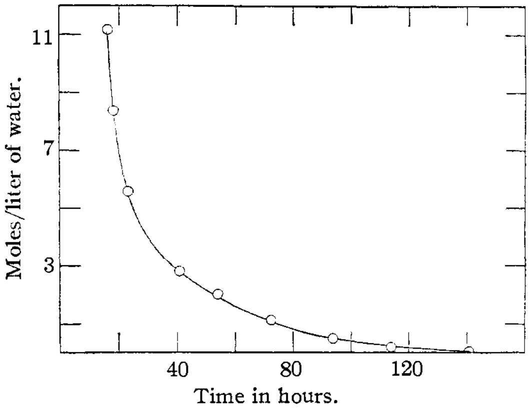

Fig. 2.—Half-time (exptl.) as a function of the concentration of added water in moles per liter (see Table I). The ratio of amine to water is approximately 5 moles of amine to quantities plotted in graph.

The isolation of a relatively high yield of the aminolytic product in a number of similar preparations makes it evident that a competitive hydrolytic process takes place at most only to a limited extent, even if the molar ratio of water to amine in the original reaction mixture is equal to or greater than 1:1.

Summary

Water has been found to catalyze the aminolysis of ethyl phenylacetate in *n*-butylamine. This effect is thought to be due to the formation of butylammonium (and hydroxyl) ions by interaction of water with the solvent.

The preparation of the N-*n*-butyl phenylacetamide from the ester and aqueous *n*-butylamine is described.

URBANA, ILL.

RECEIVED AUGUST 1, 1941