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

Acid Catalysis in Liquid Ammonia. II. Ammonolysis of Ethyl Benzoate

BY L. L. FELLINGER AND L. F. AUDRIETH

It is a well-known fact that many hydrolytic reactions are catalyzed by acids, or, in terms of the modern Brönsted concept, by the hydronium ion. The extension of our concepts to other solvent systems should therefore lead logically to the proposal that many solvolytic reactions should be susceptible to catalysis by the ion which primarily is the bearer of acidity in the specific solvent employed, namely, the "onium" ion, or the solvated proton.

Qualitatively, it has already been demonstrated that ammonium salts, acting as acids,[1] catalyze ammonolytic reactions in liquid ammonia. Only recently have any efforts been made to undertake quantitative studies of such reactions in liquid ammonia. Shatenshtein and his co-workers[2,3] showed that the ammonolysis of santonin to the corresponding amide, a reaction involving the splitting of the lactone linkage, is accelerated to a tremendous extent by the addition of various ammonium salts and ammono acids. The ammonolysis of diethyl malonate[4] has been studied in this Laboratory. The yields of malonamide were determined directly and were found to be proportional in the early stages of the reaction to the concentration of added ammonium chloride. However, this reaction proceeds so rapidly at 0° that its study was not susceptible to the degree of accuracy attained by Shatenshtein and his co-workers, who employed a polarimetric method to follow the course of their reactions. The quantitative interpretation of this reaction was further complicated by the fact that ammonolysis proceeds through the intermediate ethyl malonamate stage as indicated by the following scheme

$$CH_2(COOC_2H_5)_2 \xrightarrow{NH_3} CH_2(COOC_2H_5)(CONH_2) \xrightarrow{NH_3} CH_2(CONH_2)_2$$

Preliminary experiments indicated that the reaction between ethyl benzoate and ammonia could be subjected to an accurate quantitative study. Ammonolysis takes place in accordance with the equation

$$C_6H_5COOC_2H_5 + NH_3 \longrightarrow C_6H_5CONH_2 + C_2H_5OH$$

The rate of formation of benzamide was found to be accelerated markedly by the addition of ammonium salt. This paper presents the results of a quantitative study of the ammonolysis of ethyl benzoate at 0 and 25° in the presence of various ammonium salts.

Experimental

Experimental Procedure.—Pyrex glass tubes (16 × 300 mm.) were sealed at one end to form elongated test-tubes. Five ml. of pure ethyl benzoate (0.035 mole) was pipetted into each tube. Where the experiments were carried out in the presence of catalyst, a weighed quantity of the ammonium salt was next added. For salts other than ammonium chloride, the amount added was the molar equivalent of 0.5 g. of ammonium chloride (0.00935 mole). The tubes containing the ethyl benzoate and catalyst were cooled thoroughly in a solid carbon dioxide-acetone bath. Anhydrous liquid ammonia was then siphoned into each tube to give a total volume of 25 ml. (approximately 0.82 ± 0.03 mole of ammonia. With the contents of the tube entirely below the surface of the cooling bath, the upper end was sealed off. The tubes so prepared were allowed to warm slowly to the desired temperature and the contents thoroughly mixed to produce homogeneity of solution. The starting times of the reactions were taken as the times of mixing.

At certain time intervals, tubes of each series were removed, either from the ice-water bath or from the thermostat kept at a temperature of 25°, and immediately cooled in a carbon dioxide-acetone bath. The tubes were then opened, inserted through closely fitting rubber stoppers into filter flasks, and the contents allowed to run into the containers. After the ammonia had been removed by evaporation and gentle heating with the application of

TABLE I

AMMONOLYSIS OF ETHYL BENZOATE

(moles $C_6H_5COOC_2H_5 = 0.035$; moles $NH_3 = 0.82 \pm 0.03$)

Series	Catalyst	Mole catalyst used	Temp., °C.	Reaction velocity constant	Half-time of reaction in hours, where $\frac{a}{a-x} = 2$
a	....	.....	25	0.00014	~5000
b	NH_4Cl	0.00935	0	.000786	882
c	NH_4Cl	.00935	25	.00272	255
d	NH_4Cl	.01870	0	.00160	433
e	NH_4Cl	.01870	25	.00576	120
f	NH_4Br	.00935	25	.00208	333
g	NH_4ClO_4	.00935	25	.00155	447
h	$C_6H_5COONH_4$	.00935	25	.00336	206

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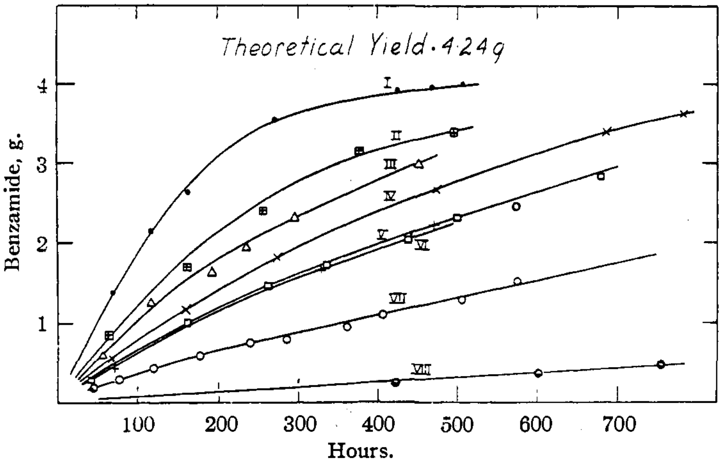
[1] For a discussion of ammonium salts as acids in liquid ammonia, see Franklin, "Nitrogen System of Compounds," A. C. S. Monograph, 1935, Reinhold Publishing Corporation, New York City, p. 26.

[2] Shatenshtein, *et al.*, THIS JOURNAL, **59**, 432 (1937).

[3] Shatenshtein, *et al.*, *Acta Physicochim.*, *U. S. S. R.*, **3**, 37 (1936).

[4] Slobutsky and Audrieth, *Trans. Ill. Acad. Sci.*, **29**, 104 (1936); *Proc. Nat. Acad. Sci.*, **23**, 611 (1937).



	Catalyst	Temp., °C.		Catalyst	Temp., °C.
I	1.0 g. NH_4Cl	25	V	1.0 g. NH_4Cl	0
II	1.14 g. C_6H_5COOH	25	VI	1.09 g. NH_4ClO_4	25
III	0.5 g. NH_4Cl	25	VII	0.5 g. NH_4Cl	0
IV	0.92 g. NH_4Br	25	VIII		25

Fig. 1.—Effect of time and catalyst on the ammonolysis of ethyl benzoate.

suction, low boiling petroleum ether (in which the ammonium salts and benzamide are insoluble) was added to extract the unreacted ester. The residues were filtered through tared sintered glass crucibles, washed with fresh petroleum ether, dried, and weighed to within 10 mg. The known weights of catalyst were deducted from the gross weights of precipitates to determine the net yields of benzamide.

Our experimental results are depicted graphically in Fig. 1, in which are plotted the yields of benzamide with respect to time under varying experimental conditions. Since ammonia was present in large excess (0.82 ± 0.03 mole of ammonia to 0.035 mole of $C_6H_5COOC_2H_5$), it may be assumed that its change in concentration during the course of the reaction is negligible. Consequently, the value for the expression $\log_{10} [a/(a - x)]$ was calculated for each run (where a = 0.035 = original number of moles of ethyl benzoate placed in each tube, and x = number of moles of benzamide formed at the time, t). The plots of these values *versus* time, as given in Fig. 2, demonstrate quite clearly that the ammonolysis of ethyl benzoate in liquid ammonia may be represented as a pseudo monomolecular reaction. The specific reaction constants were calculated from the formula

$$K = \frac{2.303}{t}\log_{10}\left[\frac{a}{a-x}\right]$$

A summary of the experimental data is given in Table I.

Discussion

The conversion of ethyl benzoate into benzamide by pure ammonia takes place very slowly indeed. The effect of adding various ammonium salts is to increase the value of the reaction velocity constant. In other words, these compounds behave as catalysts in that they speed up the reaction, but do not change its order.

Comparison of series (b) with (d), as well as (c) with (e), indicates that there is an approximate relationship between concentration of catalyst and the magnitude of the reaction velocity constant. Increase in concentration of catalyst brings about a proportional acceleration in the speed of the reaction. The catalytic effect of added ammonium salts is also apparent from the figures given in Column 6 of Table I, in which are noted the times required for 50% conversion of ethyl benzoate into benzamide.

Our findings verify those of Shatenshtein and co-workers. Again it is obvious that the catalytic effect of equivalent concentrations of various ammonium salts is opposite to what might be expected from a consideration of the usual physical

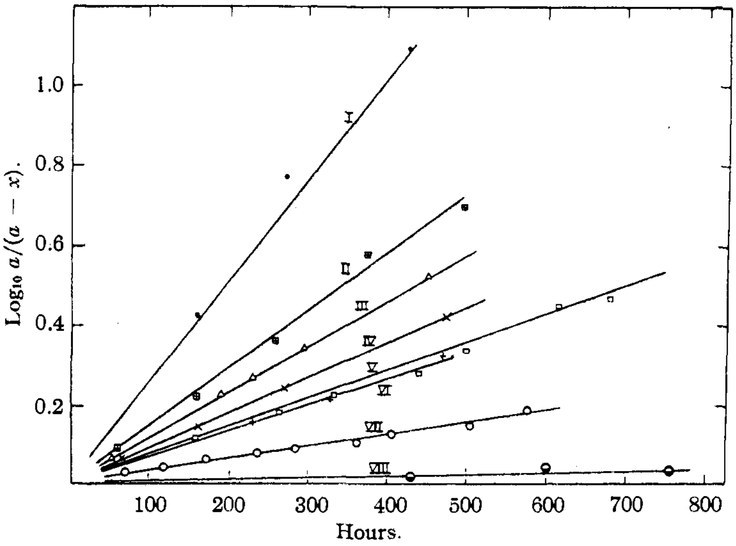


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Fig. 2.—Ammonolysis of ethyl benzoate in liquid ammonia with various compounds as catalysts.

properties of solutions of these "acids" in liquid ammonia. If the catalytic effect of the various ammonium salts were entirely dependent upon the concentration of ammonium ions, as calculated from physical data with the assumption that simple ionization is involved, one would expect the order to correspond to the anion series: $ClO_4^- > Br^- > Cl^- > C_6H_5COO^-$ (?).[5,6] For the ammonolysis of ethyl benzoate at 25° a comparison of the reaction velocity constants and half-reaction times indicates that the reverse order obtains.

Catalyst used	$C_6H_5COONH_4$	NH_4Cl	NH_4Br	NH_4ClO_4
K_c	0.00336	0.00272	0.00208	0.00155
Half-time in hours	206	252	333	447

Our experimental procedure did not permit an exact calculation of the normality of the solutions with respect to their ammonium salt content, since the solutions were made up to a volume of 25 ml. at the temperature of the solid carbon dioxide–acetone bath. For those solutions containing 0.00935 mole of ammonium salt it may be estimated that the solutions were better than 0.3 *N*. This concentration is higher than that used in most of Shatenshtein's experimental work. It lies, however, in the range where the catalytic activity of the ammonated proton is markedly influenced by the anion present. To quote Shatenshtein[2] (p. 433), "Assuming that the catalytic activity of the solvatized protons increases as the field of forces of the anions becomes stronger, one may expect that a series of acids placed in the ascending order of specific catalytic activity will be antibatic to a series of acids placed in the ascending order of electrical conductivity. . . ." Our experimental results may be regarded as confirmation of this statement. This hypothesis also is strengthened by a consideration of the properties of ammonia, which not only is a basic solvent of high proton affinity, but also one in which the effect of interionic forces is very pronounced, because of its low dielectric constant.

Summary

1. The ammonolysis of ethyl benzoate in the presence of various ammonium salts has been studied quantitatively at 0 and at 25°. The reaction has been found to be a pseudo first order reaction.

2. The catalytic effect of equivalent concentrations of various ammonium salts is given by the series

$$C_6H_5COONH_4 > NH_4Cl > NH_4Br > NH_4ClO_4$$

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(5) Shatenshtein and Uskova, *Acta Physicochim., U. S. S. R.*, **2**, 37 (1935).

(6) Gurjanova and Pleskov, *ibid.*, **5**, 509 (1936).

[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF MARYLAND]

Effect of Salts on the Acidity of Some Vanadium Pentoxide Sols[1]

BY M. M. HARING AND W. J. HART

Many studies have been made of the effect of salts on the *p*H of the intermicellar liquid of various hydrous oxide sols.[2] For the most part these studies have involved the positive sols. It was the purpose of this study to apply similar methods to the negative vanadium pentoxide sols.

Experimental

All reagents used were the purest grade obtainable and were subjected to no further purification.

Four sols were prepared, A and D by the method of Biltz[3] and B and C by the method of Müller.[4] In the case of B and C, the alternative method was used of pouring the molten oxide directly into water rather than quenching to a glass and then dispersing. No dialysis was employed with the pyrolytic sols, since the fusion at 700° for ten minutes certainly removed all volatile impurities derivable from ammonium vanadate and nitric acid. Sols A and D were both dialyzed, A for ten days with an eighteen-inch (46 cm.) length of one-inch (2.54-cm.) cellophane tubing, through which distilled water was passed at the rate of one drop per second, and D for eight days with a six-foot (1.8-meter) length of the same tub-

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(1) Abstracted from a thesis submitted by W. J. Hart to the Graduate School of the University of Maryland in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) See Whitehead, *Chem. Rev.*, **21**, 113 (1937), for a fairly extensive bibliography.

(3) Biltz, *Ber.*, **37**, 1098 (1904).

(4) Müller, *Z. Chem. Ind. Kolloide*, **8**, 302 (1911).