The ether which had been removed by distillation was found to contain acetone, identified by conversion to dibenzalacetone, m. p. 111.5–112.5°, both alone and when mixed with an authentic sample.

Oxidation of Saturated Ketones to Acids: (1) Methyl *n*-Amyl Ketone Condensation.—Five-hundredths mole of 2-methyl-5-decanone was oxidized with 0.15 mole of sodium dichromate, 0.6 mole of sulfuric acid and 250 ml. of water as previously described.[2a,16] Considerable carbon dioxide was evolved at the start and throughout the course of the oxidation. A total of 0.09 mole of acid was obtained. *n*-Caproic acid was identified in the water-insoluble acid fraction by conversion to the 2-alkyl benzimidazole,[17] m. p. 157–158°, which showed no depression when mixed with the known *n*-caproic acid derivative, m. p. 158–158.5°. Acetic acid was shown to be present in the water-soluble fraction by preparing the *p*-toluide, m. p. 146.5–147.5°, alone and when mixed with known aceto-*p*-toluide.

(2) **Methyl *n*-Hexyl Ketone Condensation.**—Five-hundredths mole of 2-methyl-5-undecanone, oxidized as above, gave 1.1 moles of total acids. *n*-Heptoic acid was identified in the water-insoluble fraction by conversion to the piperazonium salt,[18] m. p. 97–98°, which showed no depression when mixed with authentic piperazonium di-*n*-heptoate, m. p. 96–97°. Isovaleric acid was also shown to be present by preparing the piperazonium salt, m. p. 140–141°, alone and mixed with known piperazonium di-isovalerate, m. p. 140–141°. The presence of acetic acid in the water-soluble fraction was shown by preparing the *p*-toluide, m. p. 146.5–147.5°, which exhibited no depression when mixed with known aceto-*p*-toluide.

Preparation of 2-Methyl-5-decanone.—From 0.6 mole of isoamyl bromide, 0.6 mole of *n*-hexaldehyde and 0.6 mole of magnesium there was obtained 38 g. (37%) of 2-methyl-5-decanol boiling at 122–126° (28.5 mm.). Twenty-nine grams (0.17 mole) of the alcohol was oxidized to the ketone by adding dropwise, with stirring, to a mixture of 0.057 mole of sodium dichromate, 0.226 mole of sulfuric acid and 100 ml. of water. Rate of addition was controlled so that the temperature did not rise above 50°. The mixture was stirred for one hour longer, then the insoluble layer was separated, washed with sodium carbonate solution and water and dried over potassium carbonate. Distillation gave 21.5 g. (75%) of *n*-amyl isoamyl ketone, b. p. 113–118° (28.5 mm.); hydantoin, m. p. 193–194°.

Summary

1. It has been shown that isobutyraldehyde, in alkaline reaction medium, condenses through the alpha methyl carbon atom of the following methyl ketones: *n*-propyl, *n*-butyl, isobutyl, *n*-amyl and *n*-hexyl. A small fraction consisting chiefly of the unsaturated ketone resulting from methylene condensation was isolated in the methyl *n*-amyl ketone condensation.

2. Isobutyraldehyde condenses through the alpha methylene carbon atom of diethyl ketone.

3. Reduction of 2-methyl-3-decen-5-one with sodium and ethyl alcohol yielded 2-methyl-2-decen-5-ol.

4. The following new compounds have been prepared and characterized: 2-methyl-3-nonen-5-one, 2,7-dimethyl-5-octen-4-one, 2-methyl-3-decen-5-one, 2-methyl-3-undecen-5-one, 2-methyl-5-nonanone, 2,7-dimethyl-4-octanone, 2-methyl-5-decanone, 2-methyl-5-undecanone, 2-methyl-5-nonanol, 2-methyl-5-decanol, 2-methyl-5-undecanol, and 2-methyl-2-decen-5-ol.

5. The 5,5-disubstituted hydantoins of the following ketones have been prepared and characterized: 2-methyl-3-nonen-5-one, 2,7-dimethyl-5-octen-4-one, 2-methyl-3-decen-5-one, 3-*n*-butyl-5-methyl-3-hexen-2-one, 2-methyl-3-undecen-5-one, 7-methyl-4-octanone, 2-methyl-5-nonanone, 2,7-dimethyl-4-octanone, 2-methyl-5-decanone, 2-methyl-4-undecanone, and 4,6-dimethyl-3-heptanone.

6. The following new derivatives have been prepared and characterized: the nitroguanylhydrazones of 2-methyl-5-decanone and 2-methyl-5-undecanone; the 2,4-dinitrophenylhydrazone of 4,6-dimethyl-4-hepten-3-one; the semicarbazone of 2,7-dimethyl-4-octanone; the 3,5-dinitrobenzoates of 2-methyl-5-nonanol and 2,7-dimethyl-4-octanol.

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[16] Powell and Secoy, THIS JOURNAL, **53**, 765 (1931).

[17] Pool, Harwood and Ralston, *ibid.*, **59**, 178 (1937).

[18] Pollard, Adelson and Bain, *ibid.*, **56**, 1759 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

Electrolyte Catalysis in the Ammonolysis of 9-Phenyl-9-chlorofluorene by Liquid Ammonia[1]

BY P. M. WILLIAMSON,[2] ROBBIN C. ANDERSON AND GEORGE W. WATT

Studies on the ammonolysis of both esters and organic halogen compounds by liquid ammonia[3] have provided numerous examples of acceleration of the rates of these reactions by ammonium salts. Since ammonium salts behave as acids in liquid ammonia solutions,[4] it has been assumed that the observed catalytic effects are to be attributed to acid catalysis. Earlier work in these Laboratories,[5–7] has led to the suggestion[7] that catalysis by ammonium salts is fundamentally no different from similar effects produced by non-onium type salts. As a result of their studies on both ammonolytic and aminolytic reactions, Audrieth, Scott and Hill[8] have expressed tentatively this same opinion and have suggested the use of the term "electrolyte catalysis."

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[1] From the Ph.D. Dissertation of P. M. Williamson, The University of Texas, August, 1943.

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[3] For review and primary references see Fernelius and Bowman, *Chem. Revs.*, **26**, 3–48 (1940).

[4] Bergstrom, *J. Phys. Chem.*, **20**, 160 (1925).

[5] Lemons, Anderson and Watt, THIS JOURNAL, **63**, 1953 (1941).

[6] Lemons, Williamson, Anderson and Watt, *ibid.*, **64**, 467 (1942).

[7] Williamson, Anderson and Watt, *ibid.*, **65**, 49 (1943).

[8] Audrieth, Scott and Hill, *ibid.*, **64** 2498 (1942).

In an earlier paper,[7] data on the autocatalyzed ammonolysis of 9-phenyl-9-chlorofluorene and on the influence of added ammonium chloride have been presented. Work described in the present paper includes the effects produced by another ammonium salt (ammonium nitrate) and two non-onium type salts (sodium chloride and sodium nitrate). These studies provide quantitative proof of the assumption that, at least in one case, effects heretofore attributed to acid catalysis are not uniquely due to the fact that ammonium salts behave as acids in liquid ammonia but rather that these effects are more properly looked upon as typical examples of a more general electrolyte catalysis.

Experimental

Materials.—All materials were prepared and/or purified as described previously[5-7] with the exception of ammonium nitrate, in which case the C. P. reagent grade material was recrystallized three times from water, dried at 150°, and stored under anhydrous conditions.

Procedure.—Experimental data reported in this paper were obtained by procedures identical with those described by Williamson, Anderson and Watt.[7]

Data.—Sample data relating to reactions involving excess liquid ammonia and 0.3000-g. samples of 9-phenyl-9-chlorofluorene in the presence of sodium nitrate are given in Table I, while the experimental data relating to sodium chloride, sodium nitrate, and ammonium nitrate are represented graphically by Figs. 1, 2 and 3. On these graphs, each point represents the average of at least two independent measurements which were reproducible within 2%.

TABLE I

THE AMMONOLYSIS OF 9-PHENYL-9-CHLOROFLUORENE IN THE PRESENCE OF SODIUM NITRATE

$NaNO_3$, g.	Time, hr.	Vol. of soln., ml.	AgCl, g.
	Temperature, 15.08°		
0.0616	6.00	14.46	0.0490
.1229	6.00	14.52	.0600
.2460	6.00	14.67	.0786
.0616	9.00	14.43	.0673
.1229	9.00	14.50	.0811
.2459	9.00	14.70	.1022
.0616	12.00	14.33	.0848
.1230	12.00	14.48	.0988
.2458	12.00	14.48	.1193
	Temperature, 25.08°		
0.0614	3.00	14.70	0.0552
.1230	3.00	14.46	.0678
.2460	3.00	14.65	.0897
.0614	4.50	14.56	.0776
.1230	4.50	14.65	.0925
.2459	4.50	14.65	.1152
.0617	6.00	14.50	.0954
.1229	6.00	14.40	.1124
.2457	6.00	14.64	.1305

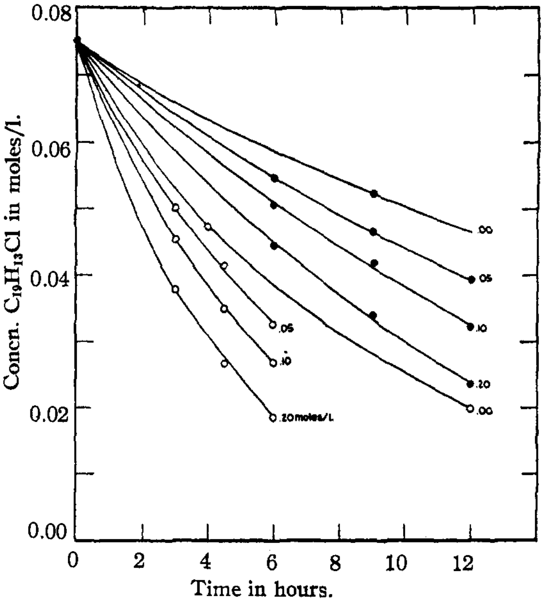

Fig. 1.—Sodium chloride: ○, at 25.08°; ●, at 15.08°.

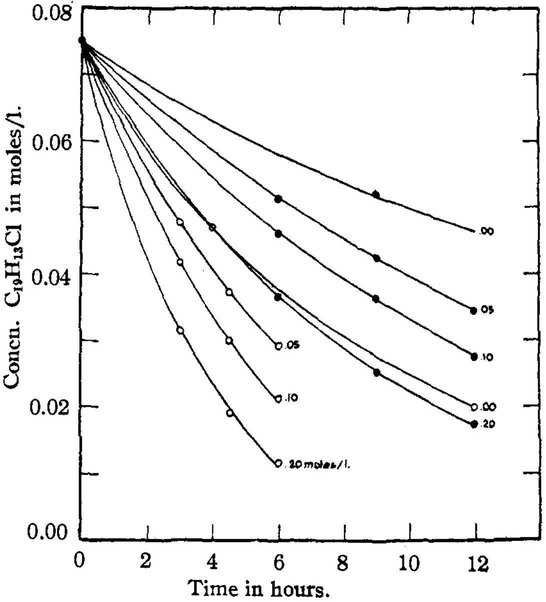

Fig. 2.—Sodium nitrate: ○, at 25.08°; ●, at 15.08°.

Discussion

The essential reaction already has been shown[7] to be the autocatalyzed formation of 9-phenyl-9-aminofluorene and ammonium chloride by the interaction of 9-phenyl-9-chlorofluorene and liquid ammonia. The results summarized in Figs. 1, 2 and 3 show that the reaction is also catalyzed by ammonium nitrate, sodium chloride, and sodium nitrate. Since preliminary calculations indicated that the catalytic effect is directly proportional to the concentration of the catalyst, the rate equation for the catalyzed reaction was concluded to be of the form

$$-dC_{C_{19}H_{13}Cl}/dt = k_1(a - x) + k_2(x)(a - x) + k_3c(a - x)$$

where a = the initial concentration of 9-phenyl-9-chlorofluorene, x = moles/l. of 9-phenyl-9-chlorofluorene ammonolyzed at time t, c = concentration of some added electrolyte other than ammonium chloride, and k_1, k_2 and k_3 are, respectively, reaction velocity constants for the un-

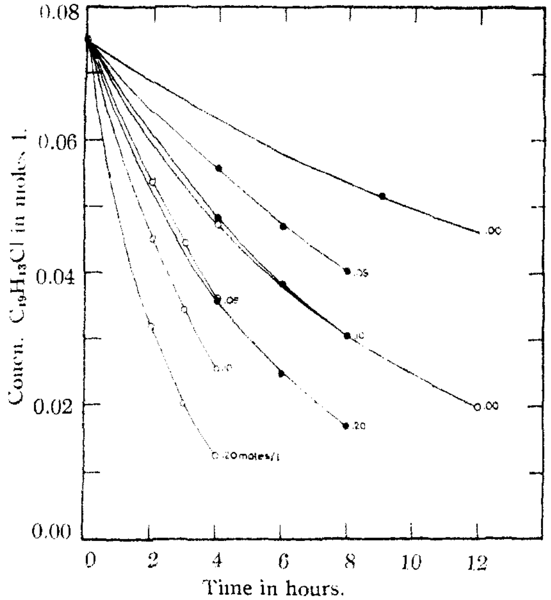

Fig. 3.—Ammonium nitrate: O, at 25.08°; ●, at 15.08°.

catalyzed reaction, the reaction catalyzed by ammonium chloride, and the reaction catalyzed by the second electrolyte.

Evaluation of Velocity Constants.—Assuming that $x = 0$ when $t = 0$, integration of the rate equation leads to the expression

$$\log \frac{ack_3 + ak_1 + ak_2x}{-cxk_3 + ack_3 - k_1x + ak_1} = \frac{(k_1 + ak_2)t + k_3ct}{2.3026}$$

Values of a, c, x and t were provided by the experimental data and k_1 and k_2 have been evaluated previously[7] under the conditions of the present experiments. Values for k_3 were therefore determined by setting

$$y_1 = \log \frac{ack_3 + ak_1 + ak_2x}{-cxk_3 + ack_3 - k_1x + ak_1}$$

and

$$y_2 = \frac{(k_1 + ak_2)t + k_3ct}{2.3026}$$

Different assumed values for k_3 were used to evaluate y_1 and y_2. These were then plotted against the corresponding values of k_4. The intersection of the two curves determined a value of k_3 for the set of data used. For each added electrolyte at a given temperature, nine such values were determined. These were then averaged by the method of least squares.

The resulting values of the various velocity constants are summarized in Table II. By use of these constants, values for x under different experimental conditions were calculated and, in general, these values agreed with the experimental data within 2–3%. Values of k_3 decrease consistently with increase in the concentration of the electrolyte (*e. g.*, 0.2690 in 0.05 M NaCl, 0.2536 in 0.1 M, and 0.2302 in 0.2 M). This trend is not surprising since the electrolyte is probably not completely dissociated in the liquid ammonia solutions. The value c, used in calculating k_3, should, therefore, be corrected by the use of an activity coefficient. Quantitative data on activities of the various solutes in liquid ammonia are not available but there is good qualitative evidence from conductance data, etc.,[9] that the probable changes in these activities are sufficient to account for both the magnitude and direction of the variations in the calculated values of k_3.

TABLE II

VELOCITY CONSTANTS AND APPARENT ENERGY OF ACTIVATION

Catalyst	Velocity constants (15.08°C.)	Velocity constants (25.08°C.)	Energy of activation, cal./mole
None	0.0349	0.0807	14,300
NH_4Cl	.409	.953	14,400
NaCl	.242	.694	17,900
$NaNO_3$	.405	1.012	15,600
NH_4NO_3	.690	1.638	14,800

Energy of Activation.—Values for the *apparent* energy of activation were calculated from the rate constants at 15.08 and 25.08° using the Arrhenius equation. These results are summarized in Table II. The values given are all reproducible to within ±800 cal./mole.

Because of experimental difficulties, including the high vapor pressure of ammonia at elevated temperatures and the very limited solubility of 9-phenyl-9-chlorofluorene at lower temperatures, it was not feasible to study the influence of variation of temperature over a wide range. Accordingly, values obtained by assuming the applicability of the Arrhenius equation do not provide an adequate basis for definite conclusions as to the mechanism of the catalytic effect. Nevertheless, it is significant that in no case is the energy of activation lower than that for the uncatalyzed reaction. This same effect has been observed previously for a number of other ammonolytic reactions.[6] The results indicate clearly that the ordinary concept that catalysis involves a lower energy of activation is not necessarily applicable to catalysis of ammonolytic reactions in liquid ammonia.

Electrolyte Catalysis.—The results summarized in Figs. 1, 2 and 3 show that the ammonolysis of 9-phenyl-9-chlorofluorene is catalyzed not only by salts which behave as acids in liquid ammonia but also by certain non-onium salts. The rate of reaction in the presence of sodium nitrate is even greater than in the presence of ammonium chloride.

Since, in the experiments involving added non-onium type salts, ammonium chloride must always be present as a product of the ammonolytic reaction, it might be suggested that the observed change in rate of reaction is a result of a change in the activity of the ammonium chloride. Shatenshtein and Markova[10] have attributed the in-

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(9) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(10) Shatenshtein and Markova, *Acta Physicochim.* (U. S. S. R.), 11, 131 (1939).

fluence of non-onium type salts upon the "acid-catalyzed ammonolysis" of pilocarpine to the resultant change in the activity of the acid. Such an explanation is certainly not tenable in the present case. The form of the rate equation indicates that there is a second catalytic effect which is additive to that of the ammonium chloride. The quantity of ammonium chloride present varies continuously, but there appears to be no correlation whatever between this variation and the observed catalytic effect. The total electrolyte concentration undoubtedly has some effect on the activity of the acid, but it is not to be expected that the addition of sodium nitrate would change the activity more than would the addition of an equivalent quantity of ammonium chloride.

Comparison of the data for sodium and ammonium salts indicates that the ammonium salts are slightly more effective catalysts than are the corresponding sodium salts. It is possible that the actual catalysts are the ammonium and sodium ions which might distort materially the carbon–chlorine bond. Comparison of the chlorides and nitrates does not, however, show any consistent variation for the different cations. This lack of consistency may arise simply from the fact that the activities of the various salts at the same concentration are different. However, it is also possible that the associated ion-pairs of a salt such as sodium chloride, which should have a large dipole moment, may influence the activation of a carbon–halogen bond in liquid ammonia and thus tend to catalyze the ammonolytic cleavage. Unfortunately, quantitative data on activities are not available and these possibilities cannot be tested at present.

After completion of the present experiments, there became available a publication in which Markova and Shatenshtein[11] describe what might appear to be a rather comprehensive study of the kinetics of the ammonolysis of organic compounds involving carbon–halogen bonds. It is impossible to evaluate their results effectively since no information is given with regard to the experimental methods employed, even though time intervals of less than five minutes were involved in some measurements while in others two liquid phases were present in the reaction mixtures. So far as one can determine from their publication, all rate constants were calculated using the equation for a first order reaction, yet in some experiments equimolar quantities of halide and liquid ammonia were used. It was assumed by Markova and Shatenshtein that the sole reaction involved in each rate measurement was the formation of the primary amine. Fernelius and Bowman[3] call attention to numerous cases of the formation of secondary and tertiary amines in the ammonolysis of alkyl halides. Otto and Watt[12] have found that the ammonolysis of ethyl iodide (one of the compounds studied by Markova and Shatenshtein) at 0° yields 48.8% ethylamine, 31.8% diethylamine, and 18.4% triethylamine.

Aside from these questionable aspects of the work of Markova and Shatenshtein, it is of interest here to observe that their results indicate qualitatively that non-onium type salts such as sodium bromide and lithium, sodium, calcium, strontium, and barium nitrates may all, at certain concentrations, catalyze the ammonolysis of ethyl chloride more effectively than ammonium nitrate. This fact is hardly consistent with their viewpoint that the catalysis is fundamentally a function of the acid present.

In view of the results obtained in the present study, it becomes important to determine whether other salts, particularly those of different charge type, will show catalytic effects similar to those exhibited by the sodium salts. Quantitative data are also needed on the influence of non-onium type salts upon the ammonolysis of organic halogen compounds involving other than carbon–chlorine bonds. Studies designed to provide such information are now in progress in these Laboratories.

Summary

1. The influence of sodium chloride, sodium nitrate and ammonium nitrate upon the rate of ammonolysis of 9-phenyl-9-chlorofluorene has been described. Values for the reaction velocity constants and energy of activation have been recorded.

2. It has been shown that this reaction is subject to electrolyte catalysis by ammonium salts and by non-onium type salts as well. The bearing of this fact upon earlier theories of acid catalysis has been discussed.

3. Attention has been directed to certain questionable aspects of related work described by Markova and Shatenshtein.

AUSTIN, TEXAS RECEIVED AUGUST 9, 1943

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[11] Markova and Shatenshtein, *Compt. rend. acad. sci. U. R. S. S.*, **35**, 68–70 (1942); *cf. Chem. Abs.*, **37**, 1321 (1943).

[12] Otto and Watt, forthcoming publication.