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

The Kinetics of the Ammonolysis of 9-Phenyl-9-chlorofluorene by Liquid Ammonia

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The experiments described in this paper represent a continuation of previously reported studies on the kinetics of the ammonolysis of organic halogen compounds[1,2] and are concerned with the ammonolysis of 9-phenyl-9-chlorofluorene, which has been shown to undergo slow ammonolysis at or above room temperature.[3]

Experimental

Materials.—All materials were prepared or purified as described previously,[1] with the exception of 9-phenyl-9-chlorofluorene which was prepared and purified as follows. By the method of Huntress and co-workers,[4] fluorene was oxidized to fluorenone (in 66% yield) which was then converted to 9-phenyl-9-hydroxyfluorene (in 64% yield) by the procedure of Ullman and von Wurstemberger[5] which was modified only to the extent necessary to permit the formation of relatively large quantities. The chief modifications involved are: (a) addition of the ketone in the form of a slurry in anhydrous ethyl ether (to avoid use of excessively large quantities of solvent), (b) separation of the addition product of the Grignard reaction by filtration through cloth rather than filter paper, and (c) use of gasoline in the recrystallization of the 9-hydroxy compound. The method described by Gomberg and Cone[6] for the chlorination of the 9-hydroxy compound was found to be unsuited to relatively large scale use. Consequently, the following procedure was employed. To 200 g. of 9-phenyl-9-hydroxyfluorene and 400 ml. of dry ethyl ether (which must be free of alcohols) contained in a 3-neck flask and cooled to 5°, was added quickly and with stirring 62 ml. (10% excess) of freshly purified thionyl chloride. After a few minutes, the reaction mixture was allowed to warm to room temperature, after which the solvent and excess thionyl chloride were removed by warming the mixture while bubbling through the solution a slow stream of dry natural gas. Following almost complete removal of the solvent, the crude product was recrystallized once from a mixture of gasoline and ethyl ether, twice from dry isopropyl ether, followed by thorough washing with cold isopropyl ether and finally with petroleum ether. The yield of pure 9-phenyl-9-chlorofluorene was 81.4 g. or 38% based on the weight of the 9-hydroxy compound used. The melting point was 78.2–78.7° (cor.) as compared with the value of 79° (uncor.) reported by Gomberg and Cone[6] and 78–79° (uncor.) reported by Kliegl.[7]

Attempted Hydrolysis of 9-Phenyl-9-chlorofluorene.—Samples of pure 9-phenyl-9-chlorofluorene were not hydrolyzed upon agitation with water at room temperature over a period of ten hours. The aqueous extract failed to give a positive test (with silver nitrate solution) for chloride ion and the 9-chloro compound was recovered unchanged.

Identification of the Ammonolysis Products.—A 2.0-g. sample of 9-phenyl-9-chlorofluorene was ammonolyzed by a large excess of anhydrous liquid ammonia in a sealed tube at room temperature over a period of forty-eight hours. Following removal of the solvent, the organic product was taken up in absolute ethyl ether, the ether was then evaporated, and the resulting sirup was crystallized several times from mixtures of (a) benzene and petroleum ether, and (b) isopropyl ether and petroleum ether. The resulting 9-phenyl-9-aminofluorene melted at 80.9–81.4° (cor.); Pinck and Hilbert[3] reported a melting point of 82° (cor.).

Anal. Calcd. for $C_{19}H_{15}N$: N, 5.45. Found: N, 5.50.

The water-soluble portion of the ammonolysis product gave positive tests for ammonium and chloride ions.

Procedure.—The experimental methods described previously[1] were used together with the following modifications: (a) weighed quantities (0.3000 g.) of 9-phenyl-9-chlorofluorene and, in some cases, weighed quantities of ammonium chloride (0.0387, 0.0774, or 0.1547 g.) were transferred quantitatively to the *bottoms* of the reaction tubes before condensation of ammonia. (b) Ammonia was condensed to the level of a brass ring placed around each tube in the predetermined position such that the final volume of the solution (at the temperature of the thermostat) would be that necessary in order to have each solution 0.0750 molar with respect to 9-phenyl-9-chlorofluorene. (c) The temperature of the thermostat was maintained at 25.08 (or 15.08) ± 0.05°. (d) The reaction tubes were opened by cooling the tubes in a dry ice–acetone mixture, cutting off the tops of the tubes, and pouring the reaction mixtures into beakers cooled with dry-ice and acetone. (This procedure permitted evaporation at temperatures sufficiently low to obviate appreciable reaction following removal of the tubes from the thermostat.) (e) Chloride ion was precipitated and weighed as silver chloride.

TABLE I

AMMONOLYSIS OF 9-PHENYL-9-CHLOROFLUORENE

NH_4Cl, g.	Time, hr.	$C_{19}H_{13}Cl$, g.	Vol. of soln., ml.	AgCl, g.
		Temperature, 25.08°		
0.0000	4.00	0.3000	14.45	0.0475
.0000	12.00	.3000	14.62	.1137
.0388	4.50	.3001	14.42	.1823
.0775	4.50	.3001	14.40	.2988
		Temperature, 15.08°		
.0000	9.00	.3004	14.32	.0466
.0000	27.00	.3004	14.17	.1102
.0387	9.00	.2978	14.54	.1711
.0774	9.00	.2989	14.59	.2895

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

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

[3] Pinck and Hilbert, *ibid.*, **59**, 8 (1937).

[4] Huntress, Hershberg and Cliff, *ibid.*, **53**, 2720 (1931).

[5] Ullman and von Wurstemberger, *Ber.*, **37**, 73 (1904).

[6] Gomberg and Cone, *ibid.*, **39**, 2957 (1906).

[7] Kliegl, *ibid.*, **38**, 284' 1905).

Data.—Representative experimental results are given in Table I. Data relative to reactions involving excess liquid ammonia and 0.3000 g. samples of 9-phenyl-9-chlorofluorene, both with and without added ammonium chloride, are summarized graphically in Fig. 1. Each point on the graph represents the average of at least two independent experiments, the results of which were reproducible within 2%.

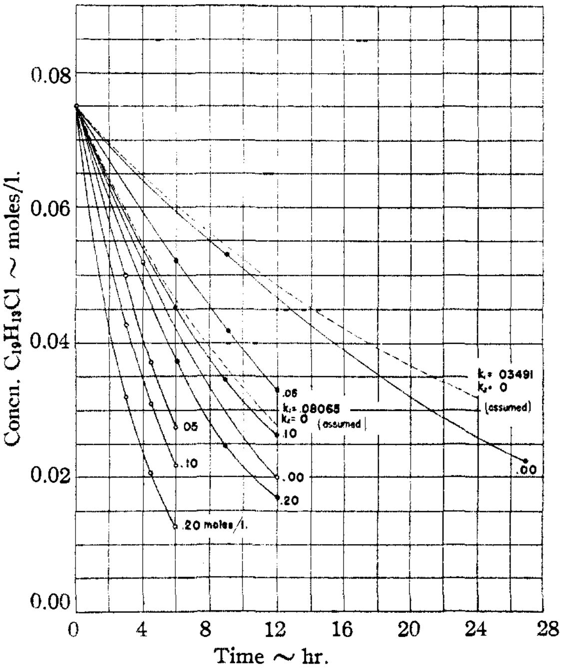
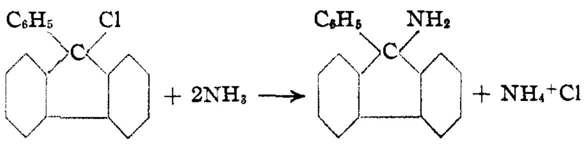


Fig. 1.—○, Temperature is 25.08°; ●, temperature is 15.08°.

Discussion

The essential reaction involved is the ammonolysis of the carbon–chlorine bond in 9-phenyl-9-chlorofluorene



Since the 9-chloro compound is not appreciably hydrolyzed at room temperature, measurement of halide ion produced over different time intervals serves as a convenient means of following the progress of the ammonolytic reaction. The results summarized in Fig. 1 show that the reaction is subject to autocatalysis by the ammonium chloride produced.

Preliminary calculations, based upon the initial rate of reaction with different concentrations of 9-phenyl-9-chlorofluorene and in the presence of varying amounts of added ammonium chloride, indicated that the simple ammonolysis in the presence of a large excess of ammonia is a pseudo first-order reaction and that the catalytic effect of the ammonium chloride is directly proportional to its concentration. Accordingly, it was concluded that the rate equation for the reaction is of the form

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

where a is initial concentration of 9-phenyl-9-chlorofluorene, x = moles/l. of 9-phenyl-9-chlorofluorene ammonolyzed at time t, c = *initial* concentration of ammonium chloride, and k_1 and k_2 are reaction velocity constants for the uncatalyzed and catalyzed reactions, respectively.

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

$$\log \frac{-k_2a(x + c) - k_1a}{(k_1 + k_2c)(x - a)} = \frac{k_1t + k_2(a + c)t}{2.3026}$$

Values of a, c, x, and t may be determined experimentally, but k_1 and k_2 cannot be determined by any simple simultaneous solution of equations. Consequently, the following method was used to evaluate these two constants: let

$$\log \frac{-k_2a(x + c) - k_1a}{(k_1 + k_2c)(x - a)} = y_1$$

and

$$\frac{k_1t + k_2(a + c)t}{2.3026} = y_2$$

A reasonable value was assumed for k_1 (*e. g.*, let $k_1 = 0.02$). Different assumed values for k_2 were then used (*e. g.*, let $k_2 = 0.42$ and $k_2 = 0.43$) and y_1 and y_2 were calculated. These values of y_1 and y_2 were plotted against the corresponding values of k_2. The intersection of the two curves thus drawn determined the point at which the value for k_2 corresponds to $k_1 = 0.02$. By repeating this process, values of k_2 corresponding to $k_1 = 0.04$, $k_1 = 0.06$, etc., were determined. The values of k_1 and k_2 were then plotted against one another and a graph which is essentially a straight line was obtained. Accordingly, k_1 and k_2 were related by a simple expression $k_2 = m + nk_1$, and the method of least squares was used to determine the values of the constants m and n.

In a similar manner, equations relating k_1 and k_2 for each set of experimental values of a, c, x, and t were set up. The entire group of equations was then solved simultaneously for k_1 and k_2, using the Gauss[8] method of substitution. The final rate constants so obtained are listed in Table II.

TABLE II

REACTION VELOCITY CONSTANTS

Temp., °C.	k_1, hr.$^{-1}$	k_2, [(moles/l.)$^{-1}$], hr.$^{-1}$
15.08	0.03491 ± 0.00004	0.409 ± 0.005
25.08	0.08065 ± 0.00003	0.953 ± 0.005

These constants were then tested by calculating values of x for various experimental conditions and comparing with the observed values. Some typical results are given in Table III. In general, the observed and calculated values agree within 4% or less.

Energy of Activation.—The apparent energy of activation was calculated from the ratios of the rate constants at 15.08 and 25.08°, using the Arrhenius equation. For the uncatalyzed ammonolysis, $E_1 = 14{,}300 \pm 700$ cal./mole, and for the catalyzed reaction, $E_2 = 14{,}400 \pm 800$ cal./mole.

Mechanism of Reaction.—The apparent order of the initial reaction and the increase in rate in the presence of ammonium chloride indicate that the uncatalyzed ammonolysis probably involves a bimolecular reaction between 9-phenyl-9-chlorofluorene and ammonia.

The actual mechanism of the autocatalysis by ammonium chloride cannot be determined at present, because too little is known concerning the nature and activities of the solutes in liquid ammonia solutions. It is of interest to note, however, that the values for the apparent energy of activation for the catalyzed and uncatalyzed reactions are essentially the same. The influence of ammonium chloride, therefore, is not the result of a decrease in the energy of activation. This is wholly in accord with results previously recorded[2] for several other ammonolytic reactions.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED VALUES OF x

c, moles/l.	t, hr.	a, moles/l.	x (obs.), moles/l.	x (calcd.), moles/l.
		Temperature, 25.08°		
0.0000	4.00	0.0751	0.02293	0.02307
.0000	12.00	.0742	.05478	.05440
.0503	4.50	.0753	.03792	.03645
.1005	4.50	.0753	.04438	.04473
.2010	4.50	.0754	.05477	.05623
		Temperature, 15.08°		
.0000	9.00	.0759	.02271	.02280
.0000	27.00	.0767	.05426	.05555
.0498	9.00	.0741	.03232	.03176
.0992	9.00	.0741	.03928	.03945
.1964	9.00	.0736	.04888	.05016

It seems likely that the influence of the ammonium chloride upon the rate is not simply a case of "acid catalysis," but that it involves some sort of general salt effect. Experimental tests of the effects produced by other salts, particularly those which do not contain the ammonium ion, may shed further light upon this question. Such experiments are now in progress.

Summary

1. Improved methods for the chlorination of 9-phenyl-9-hydroxyfluorene and the purification of the resulting 9-phenyl-9-chlorofluorene have been described.

2. The ammonolysis of 9-phenyl-9-chlorofluorene by liquid ammonia has been shown to be a pseudo first-order reaction involving autocatalysis by ammonium chloride.

3. Values for the reaction velocity constants, and energy of activation for both the catalyzed and uncatalyzed reactions have been recorded.

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[8] Brunt, "The Combination of Observations," Cambridge University Press, Cambridge, England, 1923, pp. 75–89.