4. A general scheme for the mechanism of acid catalyzed reactions of ortho esters, imidic esters, and amidines has been outlined and the relationships of these three types of compounds have been pointed out in terms of this scheme.

AUSTIN, TEXAS RECEIVED DECEMBER 21, 1949

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

The Molecular Association of Diarylformamidines

BY ROYSTON M. ROBERTS

The structure of the compounds produced by the reaction of aromatic amines with ethyl orthoformate, which had long been considered to be N,N'-diarylformamidines (I), was questioned by Post[1] who pointed out that elementary analysis data fitted equally well orthoformamide structures (II). Apparent evidence for the latter structure soon came from Post's laboratory in the form of cryoscopic molecular weight data.[2] The identification of these compounds with the orthoformamide structure was quickly challenged by Backer and Wanmaker,[3] however, who showed that the analyses of salts of the bases corresponded to formamidine structures, and more recently by Knott and Jeffreys,[4] who presented further conclusive proof that these compounds are indeed formamidines. Before the paper of Knott and Jeffreys appeared, we had reached the same conclusion based on some of the same experimental data; e. g., the formation of diarylformamidines in high yields from N-arylformimidates and aromatic amines,[5] and we had begun an investigation of the results reported by Lewis, Krupp, Tieckelmann and Post.[2] We thought that the high molecular weight values reported by these workers might be due to molecular association in solution, and we proposed two tests to show if this were the case: (1) determination of the neutralization equivalent of the hydrochloride of one of these bases by direct titration, and (2) cryoscopic molecular weight determinations *at different concentrations*.

$$\underset{\text{I}}{\mathrm{RN{=}CHNHR}} \qquad\qquad \underset{\text{II}}{\mathrm{(RNH)_3CH}}$$

The neutralization equivalent of the base hydrochloride should be independent of the degree of association and should show the formula weight of the molecule associated with one equivalent of hydrogen chloride. Lewis, *et al.*, claimed that titration of the product from aniline and ethyl orthoformate was impossible because it dissolved in hydrochloric acid very slowly. However, we found that the hydrochloride may be prepared readily by passing dry hydrogen chloride into a benzene solution of the base; the salt is reasonably soluble in water and may be titrated with sodium hydroxide to a sharp end-point. The neutralization equivalents found in three titrations were all within 1% of the calculated value for N,N'-diphenylformamidine hydrochloride.

Knott and Jeffreys[4] reported Rast molecular weight determinations which checked fairly well for N,N'-diphenylformamidine, and they suggested that the high values of Lewis, *et al.*, must be due to association, possibly to a dimeric structure. Hunter and Marriott,[6] in their extensive survey of compounds which exhibit molecular association through hydrogen bonds, investigated several N,N'-diarylacetamidines and found them to be only slightly associated in naphthalene at its freezing temperature. However, it might be expected that more association would occur at the lower freezing temperature of benzene, the cryoscopic solvent used by Lewis, *et al.* The molecular weights reported by them for the product from aniline and ethyl orthoformate were 293 ± 6 and 267 ± 3 (using 4.9 as the cryoscopic constant). The first value is very close to the formula weight of $(C_6H_5NH)_3CH$ (289); the concentration in this experiment was 1.76 g. solute/100 g. solvent. The concentration in the other experiment was not specified. The other compounds investigated by these workers were those derived from *o*-, *m*- and *p*-chloroaniline; the molecular weights found were 392 ± 4, 393 ± 4 and 393 ± 4, respectively (calculated for $(ClC_6H_4NH)_3CH$, 393), and no data regarding concentration were given.

We have now determined the apparent molecular weight of N,N'-diphenylformamidine, N,N'-di-*o*-chlorophenylformamidine and N,N'-di-*p*-chlorophenylformamidine in benzene and in naphthalene at various concentrations. The results are collected in Tables I and II and are presented graphically in Figs. 1 and 2. The formula weights of the compounds are given after the names.

The slight solubility of the chlorine-containing compounds in benzene at its freezing temperature severely limits their investigation in this solvent; at concentrations slightly higher than those in Table I, crystallization of solute occurred.

The data indicate that N,N'-diphenylformamidine and N,N'-di-*p*-chlorophenylformamidine are

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[1] H. W. Post, "The Chemistry of the Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943, p. 92.

[2] Lewis, Krupp, Tieckelmann and Post, *J. Org. Chem.*, **12**, 303 (1947).

[3] Backer and Wanmaker, *Rec. trav. chim.*, **67**, 257 (1948); **68**, 247 (1949).

[4] Knott and Jeffreys, *J. Org. Chem.*, **14**, 879 (1949).

[5] Roberts, THIS JOURNAL, **72**, 3603 (1950).

[6] Hunter and Marriott, *J. Chem. Soc.*, 777 (1941).

TABLE I

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS IN BENZENE, K_f, 5.12

Concn., g. solute per 100 g. solvent	Apparent mol. wt.	Concn., g. solute per 100 g. solvent	Apparent mol. wt.
N,N′-Diphenylformamidine, 196		N,N′-Di-*o*-chlorophenylformamidine, 265	
0.42	238	0.98	259
.49	224	1.64	261
.87	252		
.94	259		
1.20	260		
1.31	268	N,N′-Di-*p*-chlorophenylformamidine, 265	
1.32	264		
1.75	281	0.69	315
1.87	280	1.02	342
2.11	282	1.03	335
2.19	286		
2.66	291		
3.01	295		

TABLE II

CRYOSCOPIC MOLECULAR WEIGHT DETERMINATIONS IN NAPHTHALENE, K_f, 6.9

Concn., g. solute per 100 g. solvent	Apparent mol. wt.	Concn., g. solute per 100 g. solvent	Apparent mol. wt.
N,N′-Diphenylformamidine, 196		N,N′-Di-*p*-chlorophenylformamidine, 265	
0.48	205	0.98	267
1.19	211	1.66	267
1.72	220	2.41	278
2.30	223	3.15	283
2.95	229	4.07	290
3.56	234		
N,N′-Di-*o*-chlorophenylformamidine, 265			
1.12	253		
1.91	258		
2.70	258		
3.44	260		
4.37	262		

extensively associated in benzene solution at 6° and appreciably associated in naphthalene solution at 80° (the coördinates of Figs. 1 and 2 are proportioned so that the slopes of the curves give a correct indication of the relative degree of association in benzene and in naphthalene). It is interesting that N,N′-di-*o*-chlorophenylformamidine appears to be only very slightly associated even at the freezing temperature of benzene. This observation recalls the much slower rate of reaction of ethyl malonate with N,N′-di-*o*-chlorophenylformamidine and N,N′-di-*o*-tolylformamidine than with the corresponding *m*- and *p*-isomers,[7] and may be ascribed to the same cause, steric interference by the atoms or groups in the ortho positions. Fisher–Hirschfelder molecular models indicate that two ortho chlorine atoms rather effectively curtain the two nitrogen atoms, and this might well reduce intermolecular N–H–N bonding.

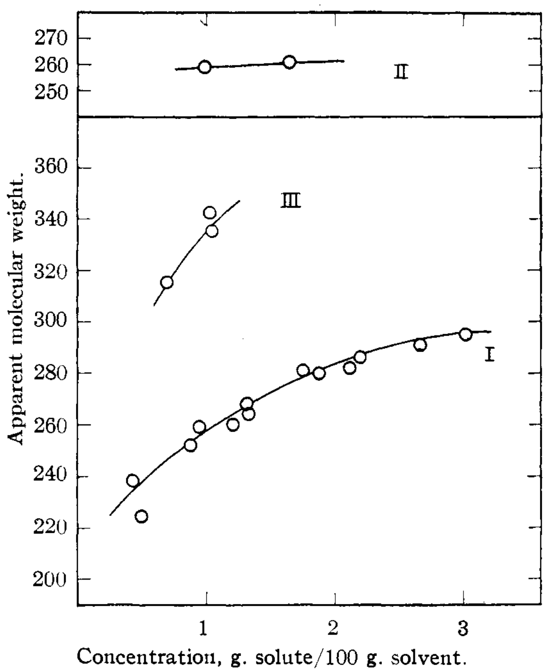

Fig. 1.—Cryoscopic molecular weight determinations in benzene: I, N,N′-diphenylformamidine; II, N,N′-di-*o*-chlorophenylformamidine; III, N,N′-di-*p*-chlorophenylformamidine.

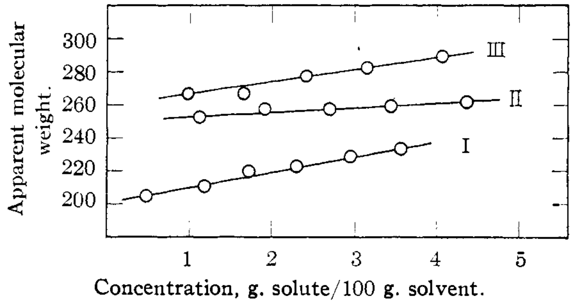

Fig. 2.—Cryoscopic molecular weight determinations in naphthalene: I, N,N′-diphenylformamidine; II, N,N′-di-*o*-chlorophenylformamidine; III, N,N′-di-*p*-chlorophenylformamidine.

Acknowledgment.—The author wishes to express his appreciation of the capable assistance of Mr. Robert H. DeWolfe, who made many of the determinations, and of a grant from The University of Texas Research Institute which made this assistance possible.

Experimental

Neutralization Equivalent of N,N′-Diphenylformamidine Hydrochloride.—The salt was precipitated by passing dry hydrogen chloride into a solution of the base (m. p. 138.0–139.2°) in dry benzene. It was collected on a filter, washed with more benzene, and dried in a vacuum desiccator over sodium hydroxide. Samples (*ca.* 0.25 g.) were dissolved in warm water (*ca.* 50 ml.) and titrated with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. Calcd. for $C_{13}H_{12}N_2HCl$: neut. equiv., 232.7. Found: neut. equiv., 231.5, 232.8, 230.9.

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[7] Roberts, *J. Org. Chem.*, **14**, 277 (1949).

Cryoscopic Molecular Weight Determinations.—The diarylformamidines were prepared from ethyl orthoformate and the aromatic amines. They were recrystallized from dry benzene–petroleum ether mixtures or benzene alone: N,N′-diphenylformamidine, m. p. 139.0–140.1°; N,N′-di-*o*-chlorophenylformamidine, m. p. 142.2–143.4°; N,N′-di-*p*-chlorophenylformamidine, m. p. 182.7–183.6°. The benzene used was dried by azeotropic distillation and stored in a flask protected by a calcium chloride tube. The naphthalene was recrystallized from petroleum ether before use; f. p. 79.7°.

The apparatus used was essentially that of Beckmann.[8] The freezing-mixture was stirred mechanically at almost constant speed by a windshield-wiper motor. Supercooling was noted and was not excessive. When benzene was used, a slow stream of dry air was introduced through a small tube near the top of the freezing-mixture tube and passed out through the stirrer bearing, preventing the entrance of moisture. In some of the first experiments, benzene was used which had been distilled several weeks previously and had not been protected adequately from moisture; the molecular weight values were higher than those obtained in really dry benzene. This behavior was checked by using as a solvent in one experiment benzene saturated with water; the following molecular weight values were obtained at the concentrations (g. solute/100 g. solvent) indicated: 286 (0.91), 308 (1.69), 317 (2.67).[9] This may account partly for the high values of Lewis, *et al.*[2]

All the molecular weight values recorded in Tables I and II were calculated from the average of several freezing point depressions which checked closely.

Summary

Cryoscopic molecular weight determinations have been carried out with three diarylformamidines in benzene and naphthalene solutions at various concentrations. N,N′-Diphenylformamidine and N,N′-di-*p*-chlorophenylformamidine are associated in both solvents, more extensively at the lower temperature of freezing benzene, while N,N′-di-*o*-chlorophenylformamidine is not appreciably associated in either solvent. The neutralization equivalent of N,N′-diphenylformamidine hydrochloride was found to indicate the expected formula weight.

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[8] See Findlay, "Practical Physical Chemistry," Longmans, Green and Co., New York, N. Y., 1925, p. 113, and Reilly and Rae, "Physico-Chemical Methods," D. Van Nostrand Co., Inc., New York, N. Y., 3rd ed., 1939, p. 621.

[9] Wright [*J. Chem. Soc.*, 683 (1949)] found that the presence of water in benzene increased the association of carboxylic and sulfinic acids.

AUSTIN, TEXAS RECEIVED DECEMBER 27, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Fractional Separation of Zirconium and Hafnium by Extraction with Trifluoroacetylacetone[1]

BY BOYD G. SCHULTZ[2] AND EDWIN M. LARSEN

Zirconium and hafnium were successfully separated by extracting a hydrochloric acid solution of the ions with a benzene solution of trifluoroacetylacetone. The zirconium was preferentially extracted into the benzene phase as the chelate compound, tetrakis-(1,1,1-trifluoro-2,4-pentanediono)-zirconium in a manner similar to that observed in the extraction of a zirconium, hafnium perchlorate solution, with thenoyltrifluoroacetone.[3]

A study of the variables involved in the extraction process showed that the diketone concentration, acid concentration, total metal ion concentration, and ion species were all factors to be considered.

Experimental

Materials.—Mixed zirconium, hafnium sulfate solutions were obtained from fractions available in this Laboratory. Stock solutions were prepared for extraction by precipitating the hydrated oxides with a slight excess of aqueous ammonia and washing the precipitate three times with distilled water by decantation. The precipitate was separated from its supernatant liquid by centrifugation, redissolved in hydrochloric acid and reprecipitated with aqueous ammonia. This process was repeated three times to ensure the absence of all anions other than chloride. The hydrated oxide was then dissolved in a measured amount of standard hydrochloric acid and diluted to the desired volume with water. A total oxide analysis was run on the resulting solution and, from this and the other known data, the normality of the resulting solution was calculated.

Tracer hafnium^{181},[4] used in following the hafnium in the extraction process, was received as the oxide and converted to a solution of the oxychloride by dissolving the oxide in 48% hydrofluoric acid, fuming with concentrated sulfuric, and precipitating the hydrated oxide with aqueous ammonia. After the sulfate had been eliminated by successive precipitations, the hydrated oxide was dissolved in hydrochloric acid.

Trifluoroacetylacetone was prepared by a Claisen condensation between ethyltrifluoroacetate and acetone.[5] Weighed amounts of trifluoroacetylacetone, at least 99.5% pure as determined by titrating with standard sodium hydroxide solution, were dissolved in thiophene-free benzene to give solutions of the desired concentrations.

Analyses.—The Zr, Hf composition of the stock solutions was determined by selenite analysis[6] or spectrographic analysis.[7]

Oxide analyses were run to determine the total oxide content of the aqueous solutions used. These analyses were made by precipitating an aliquot of the aqueous

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[1] Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy and carried out in part under Task Order 4 of Contract N7 onr-28504 between the Office of Naval Research and the University of Wisconsin.

[2] Westinghouse Electric Corporation, Atomic Power Division, Bettisfield, Pittsburgh, Pa.

[3] Huffman and Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[4] Isotopes Branch, United States Atomic Energy Commission, Oak Ridge, Tenn.

[5] Henne, Newman, Quill and Staniforth, THIS JOURNAL, **69**, 1819 (1947).

[6] Schumb and Pittman, *Ind. Eng. Chem., Anal. Ed.*, **14**, 512 (1942).

[7] C. Feldman, Oak Ridge National Laboratory, Oak Ridge, Tenn.