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Quadridentate and Sexadentate Chelates. Some Preliminary Studies in their Preparation and Thermal Stability[1]

BY C. S. MARVEL, S. ALAN ASPEY AND EDWARD A. DUDLEY

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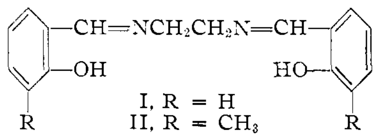
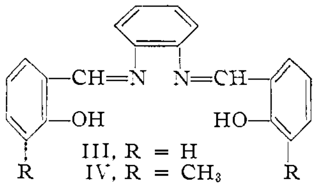
The Zn(II), Ni(II), Cu(II) and Fe(II) chelates of a variety of Schiff bases prepared from hydroxyaromatic aldehydes and diamines have been prepared and their stability toward heat in the presence and absence of air have been studied. In general Zn tetradentate chelates are the most stable in this series.

This study of some metal chelates derived from hydroxyaromatic Schiff bases was undertaken in the hope that some of these potential polymer-forming complexes might show enhanced thermal stabilities similar to known chelates. For example, copper phthalocyanine can be sublimed at 580° in nitrogen or carbon dioxide without decomposition[2] and an iron chelate of a multiple Schiff base derived from a triamine and 2-pyridine aldehyde has been distilled at temperatures above 400° without change.[3]

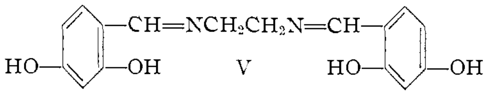
We have prepared chelates from the condensation products of *o*-hydroxyaromatic aldehydes and diamines shown in formulas I-X.



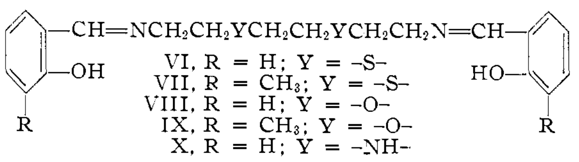
I, R = H
II, R = CH_3



III, R = H
IV, R = CH_3



V



VI, R = H; Y = -S-
VII, R = CH_3; Y = -S-
VIII, R = H; Y = -O-
IX, R = CH_3; Y = -O-
X, R = H; Y = -NH-

In this series compounds I, II and V were prepared by the methods of Diehl and his co-workers.[4] Compound III was prepared by the procedure of Pfeiffer and co-workers.[5] Compounds VI and VIII were prepared by the procedures of Dwyer, Lions and co-workers.[6] Compounds IV, VII and IX are new. Compound X was not isolated but its Zn(II), Ni(II), Cu(II) and Fe(II) chelates were obtained by the indirect procedure of Das Sarma and Bailar[7] from the free amine and the aldehyde metal chelate.

The Zn(II), Ni(II) and Cu(II) chelates of I and the Ni(II) and Cu(II) chelates of V were prepared by Pfeiffer and co-workers[8] by mixing the amine, aldehyde and metal salt or by making the metal chelate of the aldehyde and treating it with the amine. We found it more convenient to prepare the pure Schiff base and then make these chelates. The Zn(II), Ni(II), Fe(II) and Cu(II) chelates of VI have been described by Dwyer, Lions, *et al.*,[6] and their general method of preparation was used for the new Zn(II), Ni(II) Cu(II) and Fe(II) chelates of VII, VIII and IX.

The initial thermal stability tests on these chelates were made by heating the chelates in the open air at 240–260° for periods up to 48 hours. Weight losses were measured, changes in appearance noted and some of the infrared spectral changes were recorded. None of these chelates possessed the heat stability which was sought. Weight losses varied from 0.19 to 26.3% in four hours up to 5.6 to 73% in 48 hours. The hexadentates were generally less stable than the tetradentates, except for the resorcylaldehyde tetradentate derivatives which were the poorest of all. The chelates derived from Schiff bases prepared from *o*-phenylenediamine seemed to possess the greatest resistance to degradation and in this series the stability increased in the order Fe(II), Cu(II), Ni(II) to Zn(II). In the sexadentate series the order of stability varied both with the metal and the amine used.

Two additional steps were taken to study the thermal decomposition of these chelates more closely. Firstly, small samples of the three most stable sets of chelates, *i.e.*, those of Schiff bases I, III and IV, were heated for 4, 6, 8, 10, 12 and 24 hour periods and the weight loss determined in each case. It was found that the rate of decomposition varied from chelate to chelate. A short induction period was always evident. The smaller samples decomposed much more quickly. Since

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[1] The work discussed herein was performed as a part of the research project sponsored by the National Science Foundation and by the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the government synthetic rubber program.

[2] C. E. Dent and R. P. Linstead, *J. Chem. Soc.*, 1027 (1934).

[3] Private communication from Dr. F. P. Dwyer.

[4] (a) H. Diehl, C. C. Hach, G. C. Harrison and L. M. Liggett, *Iowa State Coll. J. Sci.*, **21**, 278 (1947); (b) H. Diehl, L. M. Liggett, G. C. Harrison, C. C. Hach and R. Curtis, *ibid.*, **22**, 91 (1947); (c) H. Diehl, L. M. Liggett, C. C. Hach, G. C. Harrison, L. Henselmeier, R. W. Schwandt and J. Mathews, Jr., *ibid.*, **22**, 110 (1947).

[5] P. Pfeiffer, T. Hesse, H. Pfitzner, W. Scholl and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

[6] (a) F. P. Dwyer and F. Lions, THIS JOURNAL, **72**, 1545 (1950); (b) F. P. Dwyer, N. S. Gill, E. C. Gyarfas and F. Lions, *ibid.*, **75**, 1526 (1953).

[7] B. Das Sarma and J. C. Bailar, Jr., *ibid.*, **76**, 4051 (1954).

[8] P. Pfeiffer, E. Breith, E. Luebbe and T. Tsumaki, *Ann.*, **503**, 84 (1933), and reference 5.

in general the Zn(II) chelate was the most stable in each group, a sample of the Zn chelate of Schiff base I was heated at 250° for 168 hours, when the weight loss was only 15.7%. To ascertain the type of decomposition taking place, samples of the chelates of Schiff base I were heated at 250° under nitrogen for four hours. The Zn(II) and Ni(II) chelates suffered no loss in weight, but decomposition occurred to the usual extent with the Cu(II) and Fe(II) chelates.

Infrared spectra were taken of Schiff bases, I, II, III, IV, V, VII and IX and the four metal chelates of each. The principal interest lay in the position of the conjugated C=N and the phenolic C–O bands as the chelating metal was altered (see Table III). As the phenolic C–O band in the free Schiff bases appeared to be displaced greatly, the spectra of the sodium salts of Schiff bases I and III were also investigated to obtain the normal band position of the salt-like phenolic hydroxyl group. In addition, several post-heating (48 hr.) spectra were obtained, and a comparison of these with the corresponding original spectra allows these to be divided into three classes. The first would include the four chelates of Schiff base V, where the whole region between 1000 to 1600 cm.$^{-1}$ became featureless; the second class would include the Zn(II) chelates of Schiff base I, the Zn(II) chelates of Schiff base III and the Ni(II) chelate of Schiff base IV where very little change in the spectra was noted; and the third class would include the Zn(II) chelates of Schiff base IV, where a general broadening and leveling of the bands was noted.

Preliminary experiments designed to give condensation products of these chelates with formaldehyde were not satisfactory.

Experimental Part

1,2-Bis-(2-hydroxy-3-methylbenzylideneamino)-benzene (IV).—A hot solution of 21.6 g. (0.2 mole) of *o*-phenylenediamine in 300 ml. of absolute ethanol was treated with activated charcoal and then added to 54.4 g. (0.4 mole) of 2,3-cresotaldehyde in 200 ml. of hot absolute ethanol. After heating for ten minutes, the solution was allowed to cool; bright, orange needles soon began to form. A yield of 61 g. (89%) was obtained. The melting point was 108.5–109°, and this was unchanged by further recrystallization from absolute alcohol.

Anal. Calcd. for $C_{22}H_{20}N_2O_2$: C, 76.75; H, 5.85; N, 8.13. Found: C, 76.67; H, 5.87; N, 8.27.

S,S′-Bis-[2-(2-hydroxy-3-methylbenzylideneamino)-ethyl]-ethanedithiol-1,2 (VII).—A solution of 9 g. (0.05 mole) of S,S′-bis-(2-aminoethyl)-ethanedithiol-1,2 in 50 ml. of hot absolute alcohol was added to 13.6 g. (0.1 mole) of 2,3-cresotaldehyde in 50 ml. of hot absolute ethanol. After a brief period of heating, the solution was cooled and filtered. The yield was 18 g. (87%) of bright yellow needles, m.p. 87.5–88.5°. Recrystallization from absolute ethanol did not affect the melting point.

Anal. Calcd. for $C_{22}H_{28}N_2O_2S_2$: C, 63.4; H, 6.77; N, 6.72. Found: C, 63.55; H, 6.54; N, 6.55.

O,O′-Bis-[2-(2-hydroxybenzylideneamino)-ethyl]-ethanediol-1,2 (VIII).—This was made by a modification of the method of Dwyer, *et al.*[6b] A solution of 11.1 g. (0.075 mole) of triglycoldiamine in 50 ml. of hot absolute ethanol was slowly poured into a hot solution of 18.3 (0.15 mole) of freshly distilled salicylaldehyde in 50 ml. of absolute ethanol. A yellow crystalline product soon formed. The yield was 22.4 g. (84%). Recrystallization from absolute alcohol gave material melting 46–47°. The value previously reported was 44–45°.[6b]

Anal. Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.35; H, 6.78; N, 7.86. Found: C, 67.62; H, 7.00; N, 7.77.

O,O′-Bis-[2-(2-hydroxy-3-methylbenzylideneamino)-ethyl]-ethanediol-1,2 (IX).—The procedure was identical to that for the salicylaldehyde derivative, using 11.1 g. (0.75 mole) of triglycoldiamine and 20.4 g. (0.15 mole) of 2,3-cresotaldehyde. The yield was 28.0 g. (97%). Recrystallization from absolute alcohol gave yellow crystals melting at 82–83°.

Anal. Calcd. for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 69.06; H, 7.50; N, 7.27.

Table I

Physical Properties of the Chelates

Schiff base	Metal (II)	Yield, %	Physical appearance[a]	M.p., °C.
I	Zn[b]	96	Pale yellow	>350
	Ni[c]	94	Dark red	345 d.
	Cu[c]	88	Green-black flakes	315–317 d.
	Fe[d]	10	Rust colored	
II	Zn[e]	82	Pale-yellow cryst.	>340
	Ni[c]	95	Fluffy red	>340
	Cu[c]	85	Grey-purple flakes	308
	Fe[e]	~10	Red-brown crystals	270
III	Zn[e]	98	Yellow	342–344
	Ni[c]	98	Red	352–354
	Cu[c]	91	Fine purple cryst.	318–320
	Fe[e]	100	Dark brown	323–326
IV	Zn[e]	93	Yellow crystals	348
	Ni[c]	97	Dark red	290–292
	Cu[c]	95	Fluffy brown	284
	Fe[e]	58	Fine black cryst.	287–289
V	Zn[f]	97	White	>350
	Ni[f]	73	Rust colored	>350
	Cu[f]	87	Grey	>350
	Fe[f]	99	Red-purple	>350
VI	Zn[e]	89	Pale yellow	226.5–227.5[j]
	Ni[e]	75	Brownish-green	268 d.[k]
	Cu[g]	62	Olive green	160[l]
VII	Zn[e]	100	Light yellow	250–252
	Ni[c]	100	Green-yellow	256–258 d.
	Cu[g]	79	Olive green	~115
	Fe[c]	100	Brown-black	144–147
VIII	Zn[c]	62	Pale yellow	242–244
	Ni[c]	56	Pale green	~125
	Cu[c]	43	Yellow-green	~150
	Fe[c]	61	Purple-red	150
IX	Zn[e]	80	Pale yellow	260
	Ni[e]	95	Yellow-green	261-263
	Cu[e]	96	Dark green	~245
	Fe[c]	68	Dark red-purple	~165
X	Zn[h]	81	Pale yellow	235–236
	Ni[h]	65	Light brown	200 d.
	Cu[h]	69	Blue-green	186–188
	Fe[i]		Black crystals	153 d.

[a] The chelates were obtained as powders unless otherwise stated. [b] Recrystallized by solution in pyridine and precipitated by adding ether. Dried at 140° to remove pyridine of crystallization. [c] Recrystallized by solution in chloroform and precipitated by adding ether. [d] Could not be recrystallized. [e] Purified by extracting with successive portions of chloroform, methanol, water, then methanol. [f] Purified by dissolving in 10 volumes of 10% aqueous sodium hydroxide and reprecipitating with carbon dioxide. [g] Recrystallized from benzene–petroleum ether. [h] Recrystallized from 25% methanol. [i] Purified by dissolving in a minimum amount of *n*-butyl alcohol, addition of a double volume of acetone, and precipitation with ether. [j] Reference 6a reports m.p. 224°. [k] Reference 6a reports m.p. 266°. [l] Reference 6a reports m.p. 190°.

Preparation of Chelates.—The Zn(II), Ni(II), Cu(II) and Fe(II) chelates of Schiff bases I and II were prepared by the addition of a hot solution of 0.112 mol of zinc acetate dihydrate, nickel acetate tetrahydrate, cupric acetate monohydrate in methanol and ferrous ammonium sulfate in water, respectively, to a hot solution of 0.10 mole of the Schiff base in 700 ml. of hot methanol. After cooling the mixture, the product was filtered, washed and dried in a vacuum oven. The purification procedures used for these and the following chelates and their physical properties are given in Table I, and the elementary analyses of the new chelates in Table II. The same procedure was used for the preparation of the chelates of Schiff bases VII, VIII and IX except that the amount of methanol necessary to dissolve the Schiff base had to be increased. For the preparation of 0.1 *M* amounts of the chelates of Schiff bases III and IV, the total solvent mixture was approximately 1000 ml. of methanol and 500 ml. of benzene. Also, in the case of the Fe(II) chelates of Schiff bases III, IV, VII, VIII and IX, the ferrous ammonium sulfate solution was replaced by a solution of 0.1 mole each of ferrous chloride tetrahydrate and anhydrous sodium acetate in 250 ml. of methanol.

The four chelates of Schiff base V were prepared by the addition of a hot solution of 0.04 mole of the metallic salts used for bases III, IV, VII, VIII and IX in 100 ml. of distilled water to a hot solution of 0.0375 mole of Schiff base in 700 ml. of 1.5% aqueous sodium hydroxide solution. The resulting solution was heated for 15 minutes, cooled, and filtered.

Chelates of Schiff base X were prepared by adding a cold solution of 15.2 g. of triethylenetetramine in 400 ml. of distilled water to a suspension of 0.01 mole of the appropriate disalicylyl–metal chelate suspended in 800 ml. of distilled water. The suspension was stirred and heated for 30 minutes, then cooled.

The method of preparation of the Zn(II) and Cu(II) chelates of Schiff base VI is that used for the chelates of Schiff base I. The Ni(II) and Fe(II) chelates were prepared by the method described for the chelates of Schiff base X.

TABLE II

ELEMENTARY ANALYSES OF NEW CHELATES

Schiff base	Metal (II)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
IV	Zn	64.8	63.93	4.45	4.75	6.87	6.08
	Ni	65.9	66.10	4.52	4.68	6.98	7.05
	Cu	65.1	65.00	4.47	4.57	6.90	6.94
	Fe[a]	66.3	60.84	4.56	3.99	7.03	6.20
VII	Zn	55.05	55.27	5.46	5.47	5.84	5.92
	Ni	55.8	55.48	5.54	5.65	5.92	5.43
	Cu	55.3	55.55	5.48	5.45	5.86	6.01
	Fe[a]	56.2	50.07	5.57	5.12	5.96	5.57
VIII	Zn	57.2	57.41	5.28	5.55	6.68	6.79
	Ni	58.1	58.00	5.37	5.08	6.78	6.74
	Cu[b]						
	Fe[a]	58.5	51.06	5.40	4.93	6.82	5.74
IX	Zn	59.0	60.03	5.85	6.19	6.25	6.51
	Ni	59.9	61.4	5.94	6.19	6.35	6.78
	Cu	59.2	60.73	5.89	5.83	6.28	6.60
	Fe[a]	60.3	51.49	5.98	5.06	6.39	5.22
X	Zn	57.5	57.38	5.78	5.87	13.41	13.26

[a] The iron chelates gave rather unsatisfactory analytical results, perhaps because of their ease of oxidation to Fe(III) complexes. [b] No analyses were obtained on this product due to an accident with the sample.

Infrared spectra of the chelates of seven of the Schiff bases were obtained as mentioned previously. The positions of the conjugated C=N and phenolic C–O bands of the chelates are given in Table III.

TABLE III

Compound or chelate	Conjugated C=N, in cm.$^{-1}$	Phenolic C–O, in cm.$^{-1}$
Diresorcylal ethylenediamine		
Zn(II)	1608	1358
Ni(II)	1627	1349
Cu(II)	1621	1342
Fe(II)	1625(1610)	1345
Disalicylal ethylenediamine	1637	
Na_2	1673	1348
Zn(II)	1656	1348
Ni(II)	1623	1352
Cu(II)	1651	1339
Fe(II)	1627	1310
Dicresotal ethylenediamine		
Zn(II)	1633	1318
Ni(II)	1622	1323(1342)
Cu(II)	1633	1320
Fe(II)	1629	1310(1300)
Disalicylal phenylenediamine	1616	
Na_2	1672	1336
Zn(II)	1616	1390(1328-w)
Ni(II)	1613	1378(1345-s)
Cu(II)	1613	1381(1342-w)
Fe(II)	1609	1382(1318-s)
Dicresotal phenylenediamine	1617	
Zn(II)	1618	1320
Ni(II)	1613	1340
Cu(II)	1613	1345
Fe(II)	1606	1320
Dicresotal 1,8(N)-3,6(S)[a]		
Zn(II)	1620	1320
Ni(II)	1631	1332
Cu(II)	1620	1326
Fe(II)	1610	1295(?)
Dicresotal 1,8(N)-3,6(0)[b]		
Zn(II)	1618	1321
Ni(II)	1617	1327
Cu(II)	1620	1323
Fe(II)	1613	1303–1312

[a] S,S′-bis-[2-(2-hydroxy-3-methylbenzylideneamino)-ethyl]-ethanedithiol-1,2. [b] O,O′-bis-[2-(2-hydroxy-3-methylbenzylideneamino)-ethyl]-ethanediol-1,2.

Thermal Stabilities.—The thermal stabilities of all chelates were determined by heating accurately weighed samples of about 2 g. in open Pyrex vials, 2.5 inches high and 0.5 inch in diameter, in a muffle furnace at 240–260°. After periods of 4, 8, 12, 24 and 48 hours had elapsed, the vials were removed, weighed, and returned to the furnace. The cumulative weight losses were determined, and the physical appearance of the chelates noted. The results are listed in Table IV.

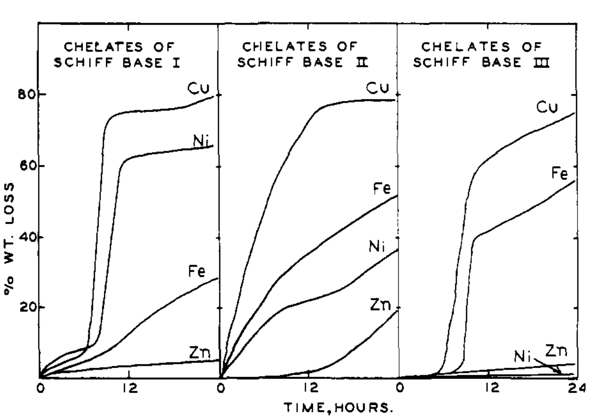

Fig. 1.—Weight loss *vs.* time curves for chelates of Schiff bases I, II and III.

TABLE IV

Chelate	M.p., °C.	Sample wt., g.	Percentage, weight loss at 240–260°					Remarks
			After 4 hr.	After 8 hr.	After 12 hr.	After 24 hr.	After 48 hr.	
Disalicylal ethylenediamine								
Zinc	>350	2.9586	0.63	0.74	0.99	4.87	17.1	Only visible change a slight, general darkening
Nickel	345	2.7589	0.45	0.9	1.55	15.7	41.9	Slight crust with gradual darkening; crust broken after 8-hr. weighing
Copper	316	2.9718	10.7	14.1	19.1	34.4	60.1	Sintered considerably within 4 hr.; formed crust which was broken up; became dark greenish-black
Iron	245	3.0480	10.7	17.3	24.6	43.9		Some darkening in color after 4 hr.; metallic discoloration developed considerably within 24 hr.
Dicresotal ethylenediamine								
Zinc	>340	2.9623	5.2	5.89	7.8	17.1	28.0	Fairly dark in color, no charring
Nickel	>340	2.0914	6.36	11.0	17.6	44.6		Considerable charring on top surface, bottom only darkened
Copper	308	2.1800	7.64	12.9	18.7	44.4		Some darkening and crust formation (which was broken up) by 4 hr. weighing; well-charred after 24 hr.
Iron	270	2.5366	7.22	9.05	11.3	25.7	52.3	Crust broken up after 4 hr. weighing; well-charred after 8 hr.
Diresorcylal ethylenediamine								
Zinc	>350	3.8661	6.96	10.5	13.8	25.1	39.5	Gradual darkening from top down; was finally a medium-brown powder; no signs of decomp.
Nickel	>350	3.4338	7.80	13.4	18.4	47.2	52.6	Ended as a dark purplish-brown powder with no charring or evident decomp.
Copper	>350	2.6719	16.1	25.8	34.1			Sample vial was spilled during the 24 hr. weighing; slight dark crust formed early; slight decomp.
Iron	>350	2.4999	17.9	27.4	35.5	54.5	73.0	Gradually changed to darker brown powder; apparently no decomp.
Disalicylal phenylenediamine								
Zinc	343	3.1042	4.94	5.02	5.3	5.4	5.60	Slight deepening of color, no other change
Nickel	353	2.2901	1.41	1.56	1.63	3.22	9.45	Change from dark red to medium brown
Copper	319	3.2355	5.32	7.5	11.0	22.7	48.2	Slight crust broken up after 8 hr.; had sintered to about 0.5 volume, turned black
Iron	325	3.0532	6.34	9.02	13.4	31.0		After 24 hr., was almost black
Dicresotal phenylenediamine								
Zinc	348	2.2243	1.14	1.1	1.21	2.69	12.6	Gradual darkening in color only change evident
Nickel	291	2.9433	0.19	0.05	0.32	5.89	16.5	Hard crust broken up after first weighing; appeared well-charred by 8 hr., but had gained weight, very slightly
Copper	284	2.9924	2.61	5.08	8.57	24.8	40.3	Slight crust broken after 4 hr., considerable darkening; very considerable decomp. after 24 hr.
Iron	288	2.9345	3.25	7.08	10.0	20.2		Formed light crust which was broken up after 8 hr.
Dicresotal triglycoldiamine								
Zinc	260	2.8652	5.31	8.20	10.5	16.6	26.1	Appeared thoroughly charred after 24 hr., initial crust was broken up after 8 hr.
Nickel	262	2.8182	6.55	10.6	15.6	24.2	40.4	Sintered considerably within 4 hr., became quite dark; completely black after 8 hr.
Copper	245	1.6101	20.6	23.3	24.8	30.0	34.2	Very dark, some charring after 4 hr., apparently advanced state of decomp. after 8 hr.
Iron	165	0.8444						Sample decomposed and foamed out of vial within first 4 hours
Disalicylal 1,8(N)-3,6(S)[a]								
Zinc	227	2.9734						Sample decomposed and foamed out of vial within first 4 hours
Nickel	267	2.2528	17.8	18.2	18.6	21.7	25.2	Hard, impenetrable crust formed early; attempts to break it up not very successful; appeared charred
Copper	190	2.7749	28.6	28.5	28.7	30.5		Formed hard, black crust which was broken up
Iron		2.7199	21.4	21.9	22.7	26.7	36.5	Very dark with evident charring after 4 hr.; appeared badly decomposed within 8; left grayish ash
Dicresotal 1,8(N)-3,6(S)								
Zinc	251	3.0312	26.3	26.1	25.8	26.4	27.1	Appeared very badly charred after only 8 hr.
Nickel	257	2.9231						Sample decomposed and foamed out of vial within four hours

TABLE IV *Continued*

Chelate	M.p. °C.	Sample wt., g.	Percentage, weight loss at 240–260° After 4 hr.	After 8 hr.	After 12 hr.	After 24 hr.	After 48 hr.	Remarks
Copper		0.4984	25.5	26.2	26.6	27.8		Became very dark, formed crust within 4 hr., appeared to be little but ash left after 8 hr.
Iron	145	1.8867	15.6	17.0	17.3	18.5		Was black, apparently decomposed within 8 hr.
Disalicylal triethylenetetraamine								
Zinc	235	3.6239						Sample decomposed and foamed out of vial within four hours

[a] 1,8(N)-3,6(S) is S,S′-bis-(2-aminoethyl)-ethanedithiol-1,2.

The more detailed thermal stability studies of the chelates of Schiff bases I, III and IV were carried out by heating accurately weighed samples of about 0.2 g. of the 12 chelates in open Pyrex sample vials, 45 × 13 mm., in a muffle furnace at 240–260° for periods of 4, 6, 8, 10, 12 and 24 hours. The samples were cooled in a desiccator, weighed, and the percentage weight losses calculated. The results are reported in the form of time–decomposition curves in Fig. 1. A sample of the Zn(II) chelate of Schiff base I was heated similarly for 168 hours after which the weight loss was 15.7%.

The stability of the chelates of Schiff base I under nitrogen were tested by heating accurately weighed samples of about 0.2 g. in Pyrex vials in a glass container which was evacuated and flushed with nitrogen several times, finally filled with nitrogen, then heated in a Woods metal-bath for 4 hours at approximately 250°. The percentage weight losses are given in Table V, along with the corresponding weight losses for samples heated open to atmosphere.

TABLE V

PERCENTAGE WEIGHT LOSSES OF THE CHELATES OF SCHIFF BASE I HEATED UNDER NITROGEN AND IN AIR

Metal	Weight loss under nitrogen, %	Weight loss in air, %
Zn(II)	0.00	1.72
Ni(II)	0.20	6.81
Cu(II)	4.93	4.73
Fe(II)	3.25	3.41

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URBANA, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANITOBA AND THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Isotope Effect in the Hydrolysis of Triphenylsilane-*d*[1]

BY CARL BRYNKO, G. E. DUNN, HENRY GILMAN AND G. S. HAMMOND

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The rate ratio, k_H/k_D, for the hydrolysis of triphenylsilane and triphenylsilane-*d* in a mixture of toluene, piperidine and water has been found to be 1.41 by kinetic measurement of the rates of hydrolysis of the separate compounds, and 1.47 by allowing the two compounds to compete in the same solution. These results agree qualitatively with those obtained by Wilzbach and Kaplan under slightly different conditions and show that the abnormal isotope effect reported earlier[2] was erroneous.

In 1951, three of the authors reported some preliminary results of an investigation into the mechanism of hydrolysis of triphenylsilane in moist piperidine[2].

$$(C_6H_5)_3SiH + H_2O \xrightarrow{\text{base}} (C_6H_5)_3SiOH + H_2$$

Separate kinetic measurements of the rates of hydrolysis of triphenylsilane and triphenylsilane-*d* indicated that the deuterium compound hydrolyzed almost six times faster than its protium analog. Such an unusual isotope effect required confirmation, and this paper records a repetition of the kinetic measurements on new samples of triphenylsilane and triphenylsilane-*d* together with experiments in which the two isotopic forms were subjected to competitive hydrolysis in one solution. The rate-ratio, k_H/k_D, was found to be 1.41 by the kinetic method and 1.47 by the competition experiments.

Before the completion of this work Wilzbach and Kaplan reported the results of similar experiments using tritium-substituted silanes,[3] and later they extended their work to include triphenylsilane-*d*.[4] Using a competition method, they found the rate-ratios for isotopically substituted triphenylsilanes to be: $k_H/k_T = 1.26$ and $k_H/k_D = 1.15$. In view of the differences in methods of hydrolysis and analysis the discrepancy between our values and these is probably not significant. Consequently, our results confirm those of Wilzbach and Kaplan and both show that the previously-reported abnormal isotope effect was erroneous.

Further investigation and discussion of the mechanism of hydrolysis of triphenylsilane in moist piperidine will be reported in a subsequent paper.

Experimental

Triphenylsilane and Triphenylsilane-*d*.—These compounds were prepared by reduction of commercial triphenylchlorosilane (Anderson Laboratories, Inc., Weston, Mich.) with lithium aluminum hydride and lithium aluminum deuteride, respectively, using the method previously described.[5] Yields of 60–64% of triphenylsilane and triphenylsilane-*d* were obtained, both melting at 44.0–44.5° (uncor.). Complete hydrolysis of the deuterated silane and analysis of its

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[1] Taken from the M.Sc. Thesis of Carl Brynko, the University of Manitoba, May, 1954. Inquiries concerning this paper should be addressed to G. E. Dunn, Chemistry Department, University of Manitoba, Winnipeg, Canada.

[2] H. Gilman, G. E. Dunn and G. S. Hammond, THIS JOURNAL, **73**, 4499 (1951).

[3] K. E. Wilzbach and L. Kaplan, *ibid.*, **74**, 6152 (1952).

[4] L. Kaplan and K. E. Wilzbach, *ibid.*, **77**, 1297 (1955).

[5] H. Gilman and G. E. Dunn, *ibid.*, **73**, 3404 (1951).