are expressed as[11]

$$E_1^0 = H_{11} + 2H_{12} + \frac{1}{2}(1\,1|1\,1) + \frac{4}{3}(1\,1|2\,2) + 2(1\,1|3\,3) + \frac{7}{6}(1\,1|4\,4)$$

$$\left.\begin{matrix}E_2^0\\E_3^0\end{matrix}\right\} = H_{11} + H_{12} + \frac{1}{2}(1\,1|1\,1) + \frac{5}{3}(1\,1|2\,2) + 2(1\,1|3\,3) + \frac{5}{6}(1\,1|4\,4)$$

$$\left.\begin{matrix}E_4^0\\E_5^0\end{matrix}\right\} = H_{11} - H_{12} + \frac{1}{2}(1\,1|1\,1) + \frac{7}{3}(1\,1|2\,2) + 2(1\,1|3\,3) + \frac{7}{6}(1\,1|4\,4)$$

$$E_6^0 = H_{11} - 2\mathrm{H}_{12} + \frac{1}{2}(1\,1|1\,1) + \frac{8}{3}(1\,1|2\,2) + 2(1\,1|3\,3) + \frac{5}{6}(1\,1|4\,4)$$

Under the approximations of formal neglect of differential overlap, electron interaction terms due to the introduction of the substituent will not enter the off-diagonal matrix elements between the molecular orbitals. When the second-order perturbation theory is applied for computing the orbital energies of a substituted benzene, the energy differences between each orbital of benzene, therefore, have considerably different values according to whether the electron interaction is included or not. Refering to Table V, the difference between the observed first ionization potentials of benzene and a substituted benzene is given by the second-order perturbation theory as follows (the terms H_{11}, $(1\,1\,|\,1\,1)$, and $(1\,1\,|\,3\,3)$ cancel)

$$I = I_B - I_S = \frac{1}{2}\left\{\frac{1}{3}\delta + \frac{\delta^2/18}{-H_{12} + \frac{1}{3}(1\,1|2\,2) - \frac{1}{3}(1\,1|4\,4)} + \frac{\delta^2/9}{2H_{12} - \frac{2}{3}(1\,1|2\,2) - \frac{1}{3}(1\,4\,|1\,4)} + \frac{\delta^2/18}{3H_{12} - (1\,1|2\,2)} + \frac{\gamma^2 \mathrm{cx}}{3(I_X - I_B)}\right\}$$

If the Pariser and Parr values are used; *i.e.*, $(1\,1\,|\,2\,2) = 7.30$, $(1\,1\,|\,4\,4) = 4.90$ e.v., and the π - π exchange integral of benzene, H_{12}, is taken as -2.39 e.v. (*cf.* ref. 3a), ΔI becomes eq. 18 of Sec. 5.

TOKYO, JAPAN

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY DEPARTMENT, TULANE UNIVERSITY, AND THE USDA SOUTHERN REGIONAL RESEARCH LABORATORY]

The Thermal Stabilities and Infrared Spectra of Some Solid Metal Salt Stabilized Diazonium Salts[1]

BY ALCUIN F. GREMILLION,[2] HANS B. JONASSEN AND ROBERT J. O'CONNOR

RECEIVED MAY 4, 1959

The chlorides of Fe(III), Zn(II), Cd(II), Sn(IV), Sb(III), Hg(II) and Bi(III) have been used to stabilize *p*-dimethylaminobenzenediazonium chloride. The rates of nitrogen evolution from the solids at elevated temperatures have been studied and the infrared spectra of the solids were recorded. A correlation has been found between the rates of nitrogen evolution and the electronic configurations of the metal ions and the electronegativities of the metal atoms. Possible modes of interaction between diazonium ion and stabilizing agent are discussed. Water in the unit cell makes the solid diazonium salt less stable. Of the principal bands in the infrared spectra the band at 2160 cm.$^{-1}$ and the out-of-plane wag of ring hydrogen are of greatest interest. This latter band appears as a well split doublet in the case of the two most stable compounds.

Introduction

Of the enormous literature on diazonium salts, in which thermal stabilities of these solid substances are reported, the work of Nesmeyanov, *et al.*,[3] covers the greatest variety of diazonium salts and inorganic stabilizing agents. Like all other reports on the stabilities they reported decomposition temperatures which were determined in the manner of melting points. The results clearly indicate an important influence of the metal salt stabilizing agents but comparisons of the results are made difficult as the decompositions occurred under various conditions. It was thought that a study of the rate of decomposition under controllable conditions would offer data more easily interpreted and more reliable.

The infrared spectra of the solids studied are also presented here.

Experimental

Preparation of Materials.—All $ZnCl_2$ stabilized diazonium salts were purchased from the Ringwood Chemical Company, Ringwood, Illinois. The other materials were prepared by stabilizing a saturated aqueous solution of *p*-dimethylaminobenzenediazonium chloride with a saturated aqueous solution of the appropriate metal salt. In the cases of stabilization with $SbCl_3$ and $BiCl_3$ the saturated stabilizing solutions were prepared with concentrated hydrochloric acid. Water and concentrated hydrochloric acid solutions of $SnCl_4$ both gave the same results. The compounds prepared were all precipitated from solution. Each precipitate was filtered, washed with 10% hydrochloric acid, pressed dry and stored *in vacuo* for several days with continuous pumping.

The *p*-dimethylaminobenzenediazonium chloride used in the preparations was obtained by destabilization of its $ZnCl_2$ stabilized derivative. Hydrogen sulfide was passed into an aqueous solution of the *p*-$(CH_3)_2N\text{–}C_6H_4\text{–}N_2Cl\cdot ZnCl_2\cdot 2H_2O$ until zinc sulfide would no longer precipitate. This required several filtrations of zinc sulfide and reuse of hydrogen sulfide. By passing in nitrogen the excess hydrogen sulfide was purged from the solution until the hydrogen sulfide odor was no longer detectable. The resulting solution was subjected to a vacuum distillation with water being removed until a saturated solution of the destabilized salt was obtained.

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[1] From a doctoral dissertation by Alcuin F. Gremillion.

[2] Monsanto Chemical Company, Lion Oil Division Research, El Dorado, Arkansas.

[3] A. N. Nesmeyanov, K. A. Kocheshkov, V. A. Klimova and N. K. Gipp, *Ber.*, **68B**, 1877 (1935).

In further designations of the materials used D indicates the *p*-dimethylaminobenzenediazonium ion and D′ indicates the *p*-diethylaminobenzenediazonium ion.

Stabilizations were accomplished with the chlorides of Fe(III), Zn(II), Cd(II), Sn(IV), Sb(III), Hg(II), and Bi(III). Attempts to stabilize by the above method were unsuccessful with Na(I), Mg(II), Ca(II), Cr(III), Mn(II), Co(II), Ni(II), Cu(II) and Ba(II).

Analysis of Materials.—Analyses for water were carried out by the Karl Fischer method.[4] The analyses for diazonium nitrogen were conducted by the method of Schaefer and Becker.[5]

Zinc and cadmium were analyzed for by the pyrophosphate method. Because of the presence of the diazonium ion the method was modified so as not to use hot solutions. Mercury, antimony and bismuth were analyzed as the sulfides. Iron was determined as the oxide after first destroying the organic material.

$(D'Cl)_2 \cdot ZnCl_2$.—When this substance (0.3526 g.) was added to 10 ml. of acetonitrile blanked with Karl Fischer reagent no discoloration of the solution resulted. *Anal.* Calcd.: H_2O, 0.00; Zn, 11.67. Found: H_2O, 0.00; Zn, 11.55.

$D'Cl \cdot ZnCl_2 \cdot H_2O$.—*Anal.* Calcd.: H_2O, 4.92. Found: H_2O, 5.00.

$DCl \cdot ZnCl_2 \cdot 2H_2O$.—*Anal.* Calcd.: H_2O, 10.12; diazo N_2, 7.87; Zn, 18.35. Found: H_2O, 10.12; diazo N_2, 7.74; Zn, 19.10.

DCl.—*Anal.* Calcd.: H_2O, 0.00; diazo N_2, 15.25. Found: H_2O, 0.00; diazo N_2, 15.10.

$DCl \cdot CdCl_2 \cdot H_2O$.—*Anal.* Calcd.: H_2O, 4.68; Cd, 29.19. Found: H_2O, 4.84; Cd, 29.20.

$DCl \cdot SnCl_4 \cdot {}^1/_2H_2O$.—*Anal.* Calcd.: H_2O, 1.99. Found: H_2O, 1.94.

$DCl \cdot HgCl_2$.—*Anal.* Calcd.: H_2O, 0.00; Hg, 43.9. Found: H_2O, 0.00; Hg, 44.9 and 45.0.

$DCl \cdot FeCl_3$.—*Anal.* Calcd.: H_2O, 0.00; Fe, 16.1. Found: H_2O, 0.00; Fe, 16.9 and 17.2.

$DCl \cdot 2SbCl_3$.—*Anal.* Calcd.: H_2O, 0.00; Sb, 38.1. Found: H_2O, 0.00; Sb, 38.2 and 38.5.

$DCl \cdot BiCl_3$.—*Anal.* Calcd.: H_2O, 0.00; Bi, 41.8. Found: H_2O, 0.00; Bi, 41.7.

Spectra.—The infrared spectra were all taken on KBr disc preparations using about 2 mg. of sample in each case. This was added to 350 mg. of powdered KBr then mixed and stirred with a Mullite mortar and pestle. Of each sample mixture 300 mg. was transferred to a Perkin–Elmer die, and the KBr disc made by pressing in a laboratory hydraulic press. The die was evacuated to about 3 mm. before pressing. The die then was subjected to a force of 2500 lb., and pressed for 10 min. after increasing the vacuum to 1 mm.

The spectra were taken with a Perkin–Elmer Model 21 double beam instrument. Each spectrum was run against a KBr reference disc after balancing the instrument with reference discs in both beams. The automatic adjustment of slit width was programmed on the instrument as follows: resolution 927, suppression 3, gain 6, response 1 and speed of 0.5 micron/min. The disc temperature in the infrared beam was about 40°.

The spectra of the same compounds in Nujol mull are generally poorer than the others.

Thermal Stabilities and the Apparatus.—The order of thermal stabilities of the compounds studied has been based upon the rates of evolution of nitrogen at a constant elevated temperature and constant pressure. The data are given in Figs. 1 and 2. The apparatus consisted of a gas buret having two side arms. One side arm was attached to a manometer containing Miriam fluid No. 3 (tetrabromoethane, density *ca.* 3). The sample tube was attached to the second side arm. This tube had two sections. The lower section was about 10 cm. long and 6 mm. inside diameter. This part of the tube contained a 0.1 to 0.2 g. sample. The upper section was 5 cm. long and 2.5 cm. in diameter. A loose glass wool plug was placed at the shoulder in this tube and above this, calcium oxide lumps were placed. These lumps were present to pick up any moisture in the apparatus and to catch any HCl that might be evolved. The bottom of the buret was attached to a valve system so that buret fluid could be removed or introduced to the buret

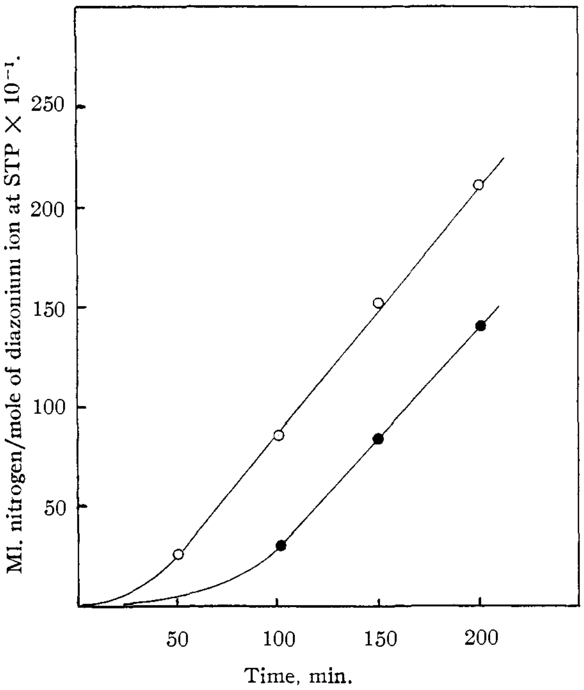

Fig. 1.—Nitrogen evolution rate plots for $DCl \cdot FeCl_3$ (O) and $DCl \cdot ZnCl_2 \cdot 2H_2O$ (●) at 88°.

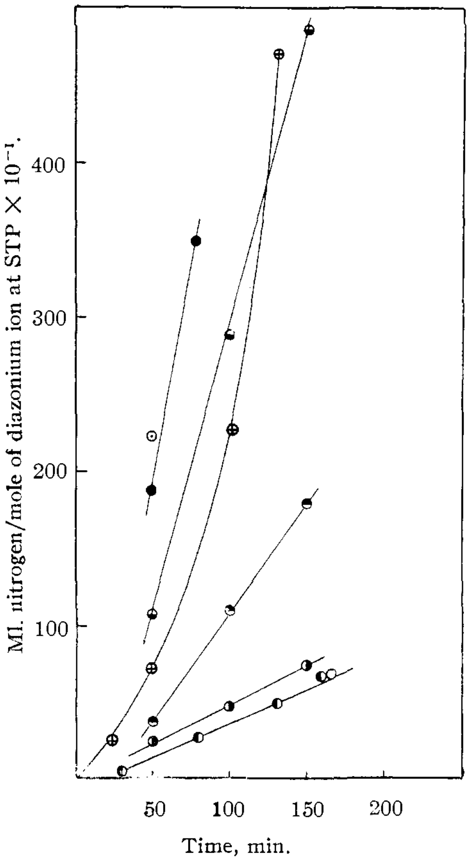

Fig. 2.—Nitrogen evolution rate plots for DCl (⊙), $DCl \cdot 2SbCl_3$ (●), $D'Cl \cdot ZnCl_2 \cdot H_2O$ (⊕), $DCl \cdot BiCl_3$ (◒), $DCl \cdot HgCl_2$ (◓), $DCl \cdot SnCl_4 \cdot {}^1/_2H_2O$ (◑), $(D'Cl)_2 \cdot ZnCl_2$ (O) and $DCl \cdot CdCl_2 \cdot H_2O$ (◐), at 98°.

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[4] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[5] W. E. Schaefer and W. W. Becker, *Ind. Eng. Chem., Anal. Ed.*, **19**, 307 (1947).

at will. With the sample in the apparatus and the fluid level in the buret at the top, the system was closed. Temperature, barometric pressure and buret reading were recorded and a container of some boiling fluid was raised around the sample tube tip containing the sample. At this point a timing device was started. At the end of a predetermined interval the boiling fluid was removed, the sample was cooled rapidly to the temperature of the small air-conditioned room and the buret was read with the manometer indicating atmospheric pressure. Throughout each experiment atmospheric pressure was maintained.

The temperature at which the sample was maintained during each run was chosen so as to give a conveniently measured rate of nitrogen evolution. The boiling fluids used were trichloroethylene and *n*-propyl alcohol. Temperature of the apparatus was maintained at ±0.1°. The buret was constructed to hold 15 ml. in the portion graduated to be read to ±0.01 ml.

The points on a given curve were obtained by determining the amount of nitrogen evolved from a sample for each of several successive time intervals.

Results

Stability in this discussion is taken as lack of ready evolution of nitrogen through thermal decomposition. At room temperature the compounds studied are stable. At 78° the iron compound and the dihydrate of the zinc stabilized diazonium salt showed no gas evolution after 100 min. At 98° these same compounds liquefied and evolved gas at too rapid a rate. They remained in the solid state at 88° and evolved nitrogen at a conveniently measured rate. The mercury compound evolved no gas in 50 minutes while at 88°. It gave the nitrogen evolution rate at 98° as shown in Fig. 2. Ninety eight degrees was a suitable temperature for all other compounds studied. A microscopic examination of each solid studied, at its respective temperature, showed no evidence of liquid being present. It appears that for these compounds there is only a small temperature range over which the nitrogen evolution rate could be studied by the method employed. Reliable energies of activation cannot be obtained from rate studies over small temperature ranges, as indicated by Hyne and Robertson.[6]

The infrared spectra of the compounds studied were taken. Figure 3 presents one of the spectra.

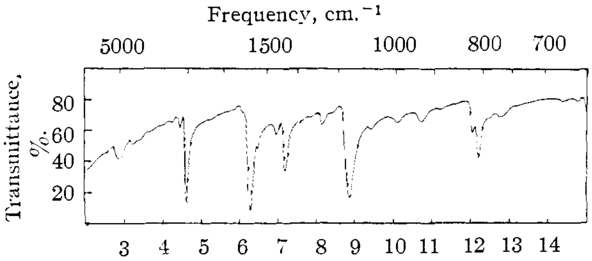

Fig. 3.—The infrared spectrum of $DCl\cdot CdCl_2\cdot H_2O$. Sample temperature in the beam, *ca.* 40°; concentration, 6.00 mg. of sample per 1000 mg. of KBr; slit width automatically adjusted by programming Perkin–Elmer Model 21 spectrophotometer with resolution at 927, suppression at 3, gain at 6, response at 1 and speed at 0.5 μ/min.

The band at 2160 ± 9 $cm.^{-1}$ appears in all spectra, including the spectrum of the unstabilized diazonium salt. This band has been attributed by Whetsel, Hawkins and Johnson[7] and by Aroney, LeFevre and Werner[8] to the multiple bond of the diazonium group.

All spectra show a strong band at 1605–1590 $cm.^{-1}$ and a medium intensity shoulder at about 1570 $cm.^{-1}$ which is in accord with Bellamy's report[9] on this band. The 1600 $cm.^{-1}$ band also has a shoulder on the high frequency side for all of the hydrates. The shoulder is most pronounced in the case of the tin compound for which this main band appears at 1590 $cm.^{-1}$. Water has three fundamental bands[10] at 3756, 3652 and 1595 $cm.^{-1}$. The second shoulder on the 1600 $cm.^{-1}$ band probably is due to water and the first shoulder has been attributed to unsaturation conjugated with the ring.

The most pronounced variations from spectrum to spectrum are the shift of the ring-hydrogen wagging frequency, given in Table III, and the appearance of this band as a doublet in the case of the two most stable compounds (Fig. 3).

Discussion

The data of Figs. 1 and 2 show curves similar to the type obtained by Vaughan and Phillips[11] for the thermal decomposition of solid 2-nitrobenzene-4-diazo-1-oxide. They interpreted their results in terms of the theory of Prout and Tompkins.[12] This theory is for decomposition of solids without partial melting. According to their theory, the decomposition of molecules of the solid crystal gives products which cause strains in the crystal resulting in crack formation. On the new surfaces more decomposition occurs. A time *vs.* volume curve characteristic of autocatalytic processes is obtained.

By this theory the ease of decomposition of the molecule determines the shape and position of the toe of the curve. This in turn determines the position on the abscissa and slope of the straight-line or near straight-line portion of the curve. As there is a fanning-out arrangement of plots for the decompositions of the present study, the positions and relative slopes of the near straight-line portions of the plots have been taken as an indirect indication of relative stabilities.

The data for the zinc compounds indicate that the greater the amount of water in the unit cell the less stable is the compound. It is assumed that a *p*-diethylamino group has essentially the same influence on the nitrogen evolution rate as a *p*-dimethylamino group. However, this does not seem an unreasonable assumption.

In arranging these compounds in order of their stabilities the above observation concerning water has been borne in mind. The following order on increasing stabilities according to the metal present

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[6] J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **33**, 1544 (1955).

[7] K. B. Whetsel, G. F. Hawkins and F. E. Johnson, This Journal, **78**, 3360 (1956).

[8] M. Aroney, R. J. W. LeFevre and R. L. Werner, *J. Chem. Soc.*, 276 (1955).

[9] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Company, London, 1954, p. 61.

[10] G. Herzberg, "Molecular Spectra and Molecular Structure: Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 207.

[11] J. Vaughan and L. Phillips, *J. Chem. Soc.*, 1560 (1947).

[12] E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, **40**, 488 (1944).

TABLE I

Metal ion	Orbital config.	Slope of near st.-line part of curve for anhy. cpd., Fig. 1 or 2	De-compn. temp., °C.
Fe(III)	KL $3s^2$ $3p^6$ $3d^5$	12.4	88
		$\gg$58.2	98
Sb(III)	KLM $4s^2$ $4p^6$ $4d^{10}$ $5s^2$	58.2	98
Bi(III)	KLMN $5s^2$ $5p^6$ $5d^{10}$ $6s^2$	36.2	98
Hg(II)	KLMN $5s^2$ $5p^6$ $5d^{10}$	14.2	98
Sn(IV)	KLM $4s^2$ $4p^6$ $4d^{10}$	<5.1	98
Zn(II)	KL $3s^2$ $3p^6$ $3d^{10}$	*ca.* 4.4	98
Cd(II)	KLM $4s^2$ $4p^6$ $4d^{10}$	<4.4	98

TABLE II

ELECTRONEGATIVITIES OF VARIOUS AUTHORS OBTAINED BY VARIOUS METHODS[a]

	Sanderson's[13] stability ratios	Allred and Rochow's[16] "absolute" values	Pauling's[17] thermal electro-negativities	Gordy's[18] electronega-tivities	Haissinsky's[19] values	Pritchard and Skinner's[20] "Best" values	Pritchard and Skinner's[20] Electroneg. using Slaters effective nuclear charge
Fe	3.27	2.505					
Sb	3.37	2.993	1.8	1.82		1.9	1.93
Bi	3.78				1.8	1.8	
Hg	3.47				1.9 (II)	1.9 (II)	
Sn	3.10	2.708	1.7	1.61	1.8 (IV)	1.8–1.9 (IV)	1.74
Zn	2.84	2.564		1.21	1.5	1.5	1.32
Cd	2.59	2.003		1.13	1.5	1.4	1.23

[a] Roman numerals indicate values for the ions of that oxidation state.

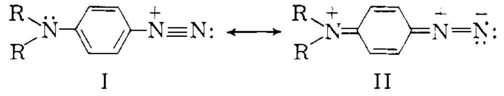
is based on Figs. 1 and 2: Fe<Sb<Bi<Hg<Sn $\cong$ Zn < Cd. The tin compound is a hemi-hydrate so that its anhydrous analog should be nearly of the same stability as the zinc compound.

In considering the temperatures of these decompositions and the positions and slopes of the plots of Figs. 1 and 2, the compounds studied and/or their anhydrous analogs divide into three groups. The iron compound is a group by itself. The antimony and bismuth compounds constitute a second group and the mercury, tin, zinc and cadmium compounds form a third group. The same grouping is obtained if conducted according to the outer orbital electronic configurations of the metal ions (Table I).

This is suggestive of the "stability ratios" of Sanderson[13,14] which are an electronegativity scale based upon the packing of electrons about the nucleus. Table II lists the metal atoms of the compounds studied in the same order as that of Table I and includes the electronegativities as given by various authors. In general, increasing electronegativity is in the direction of decreasing stability of the compounds containing these metals. The correlation is good on the lower end of the table but Fe does not correlate as well as any of the other metals. Nevertheless, if the correlation is not fortuitous it is doubtful that electronegativity of the metal atom is the only important factor.

Orbital electronic configuration is apparently also an important factor although the separation of electronegativity and electronic configuration may not be possible. According to Mulliken,[15] electronegativity depends upon orbital characteristics. Seven electronegativity scales have been used, for there remains even now some question about the correct values for some elements or the best method of obtaining electronegativities. As recently as 1958 a new scale of electronegativities[16] has been proposed.

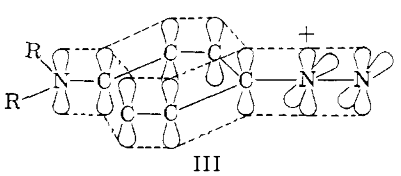
The data on thermal stabilities indicate a dependence of this property on the nature of the metal involved. Several points on the diazonium ion should be considered as possible points of interaction between metal ion and diazonium ion. The electron pair on the nitrogen remote from the ring is perhaps a point of interaction. The frequency of vibration of the diazonium group should be shifted by large variations of mass and nature of


I II

the metal ion interacting at this point. However, the observation is that for all the compounds studied the vibration frequency variation is about that of experimental error for the region near 2100 cm.$^{-1}$.

The unshared electron pair of the amino nitrogen should be considered. However, it is well known[21] that tertiary amines have little tendency to be coördinated. Coördination of this electron pair would result in less coplanarity of the bonds of the amino nitrogen. This is resisted by resonance. Resonance in the diazonium ion results in the flow of electrons away from the amino nitrogen[22] leaving it more positive and less likely to interact with a metal ion.

A simple molecular orbital picture III of the diazonium ion emphasizes the π-cloud and suggests this as the vehicle of interaction in the


III

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(13) R. T. Sanderson, *J. Chem. Educ.*, **29**, 539 (1952).

(14) R. T. Sanderson, *J. Chem. Phys.*, **23**, 2467 (1955).

(15) R. S. Mulliken, *ibid.*, **2**, 782 (1934).

(16) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).

(17) L. Pauling, "The Nature of the Chemical Bond," Chapter II, Cornell University Press, Ithaca, New York, 1939.

(18) W. Gordy, *Phys. Revs.*, **69**, 604 (1946).

(19) M. Haissinsky, *J. phys. radium*, **7**, 7 (1946).

(20) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).

(21) F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

(22) C. A. Coulson, "Valence," Oxford University Press, London, 1952, p. 246.

vicinity of the ring. This model has the merit that increasing electronegativity or vacant d orbitals leads to increased transfer of π-cloud in the direction of the metal ion. This postulated model can account for the stabilities found.

Cowdrey and Davies[23] have stated that the diazotized anisidines are more stable than benzenediazonium salts which are more stable than diazotized *o*-toluidine. Nesmeyanov's[3] data indicate that those compounds having a group on the ring which allows delocalization of an electron pair are generally the most thermally stable. A metal–diazonium ion interaction as postulated above would assist in the flow of electrons from the amino nitrogen and increase stability. However, as such an interaction increases in strength (increasing electronegativity of the metal atom) flow of electrons from the vicinity of the C–N_2^+ bond should also increase with the positive charge on the diazonium group resisting this. The result is decreased electron density in the C–N_2^+ bond and its becoming weakened. The delocalization of the amino group electron pair and the decrease of electron density in the above bond have opposite effects. When the pull of electrons away from the C–N_2^+ bond becomes large the net effect is destabilization. Considering the effect of water, only the iron compound is less stable than the *p*-dimethylaminobenzenediazonium chloride. In this study only the iron compound has incomplete outer orbitals (3d). These are well known for their coördination of electrons.

The variation of the frequency for the out-of-plane ring hydrogen wag suggests an interaction as proposed. An explanation of Table III is offered by the assumption that the metal ions position themselves over the center of the ring and in the case of the two most stable compounds the metal ions are closer to one side of the ring than the other.

TABLE III

ABSORPTION FREQUENCIES FOR RING HYDROGEN WAGGING

Metal of the compd.	Cm.$^{-1}$	% Trans.
None	818	11.6
Fe	817	10.0
Bi	820	25.0
Zn($2H_2O$)	823	26.0
Zn(H_2O)	824	18.8
Sn	826	37.0
Hg	817	11.5
Zn	821	38.5
	833	45.0
Cd	818	42.0
	829	57.5

In spite of the failure to "stabilize" with some of the metal chlorides used, it seems that the present data should be extended to include more metal ions. It is also suggested that greater insight into the interaction of metal ion with diazonium ion may be available through nuclear magnetic resonance spectroscopy.

NEW ORLEANS, LA.

[23] W. A. Cowdrey and D. S. Davies, *Quart. Rev.*, **6**, 358 (1952).

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Molecular Addition Compounds of Iodine. I. An Absolute Method for the Spectroscopic Determination of Equilibrium Constants

BY NORMAN J. ROSE AND RUSSELL S. DRAGO

RECEIVED APRIL 1, 1959

A general equation is derived for evaluating acid–base equilibria from spectroscopic data. The equation is a general one and can be applied to any acid–base system that absorbs in some region of the spectra. Application to base–iodine systems is described. The treatment requires fewer assumptions than are involved in the Benesi–Hildebrand treatment or several reported modifications of it. In this article the equation is derived, its application illustrated and the interpretation of reported data evaluated. The advantages of employing our treatment are outlined.

Introduction

The interaction between Lewis bases and iodine provides an ideal system for investigating the basicity of various electron pair donors. The addition compounds formed with iodine are soluble in non-polar solvents so their heats of formation can be determined in the absence of crystal lattice effects or extensive solvation by studying the equilibrium constant of the reaction [$B + I_2 \rightleftarrows BI_2$] as a function of temperature. These data usually are obtained from the ultraviolet spectra of the solutions. The equilibrium constant often is calculated by the method proposed by Benesi and Hildebrand[1] or some modification of it.[2-4]

In many of these studies, conclusions and explanations for observed trends are based on small differences in the heats of formation. The slight curvature obtained in the plot of ln K *vs.* $1/T$ was used[5] as evidence to support existence of several geometrical isomers. Scott[6] has been concerned with the effect of solvent on these equilibria and has obtained slightly different values for the equilibrium constant for the reaction $C_6H_6 + I_2 \rightleftarrows C_6H_6{\cdot}I_2$ in carbon tetrachloride and in pure benzene as the solvents. DeMaine,[7] on the other hand, reports no solvation effects for the equilibrium between ethanol and iodine.

In view of the importance of conclusions based on small differences in the values for the constant

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[1] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

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[4] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

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