when the reaction was well started, the mixture was added to 8.50 g. (0.350 g. atom) of magnesium in a 500-ml. three-necked flask equipped with stirrer, Dry Ice condenser protected with a drying tube, dropping funnel and gas inlet. Gaseous dimethyl ether dried by passage through a Drierite-filled tower was run in until 50 ml. of liquid had condensed. The remainder of the ethereal bromide solution was added dropwise during 100 minutes. After an additional 60 minutes, a solution of 26.2 g. (0.430 mole) of deuteroacetic acid in diethyl ether was added dropwise to the vigorously stirred Grignard mixture. After the addition was complete, the dimethyl ether was allowed to evaporate and the residue taken up in diethyl ether. The solution gave a negative test for Grignard reagent. The organic products were then separated, washed and dried in the usual manner. On distillation, 9.7 g. of starting material, b.p. 154–158° (745 mm.), $n^{25}\text{D}$ 1.5291, was recovered. The fluorobenzene-2-*d* amounted to 18.8 g. (55% conversion, 66% yield) and had b.p. 83.0–85.0° (745 mm.).

Exchange Reactions.—The deuterium–protium exchange reactions were carried out at the boiling point of liquid ammonia using an apparatus similar to that described by Schlatter[19] for sodium amide reactions except that 100-ml. flasks were employed. A solution of potassium amide in liquid ammonia was prepared in one flask by adding 1.8 g. (0.046 g. atom) of potassium metal to 25 ml. of stirred liquid ammonia containing a small crystal of ferric nitrate nonahydrate. The amide solution was then forced by air pressure into the second flask which contained 3.00 g. of the substituted deuterobenzene dissolved in 50 ml. of the liquid ammonia. The reaction mixture was stirred under reflux for the desired interval and then 4.8 g. of ammonium chloride was added. The reaction mixture was diluted with 25 ml. of ether and the ammonia allowed to evaporate. The ethereal solution was boiled under reflux for 10 minutes to drive off any residual ammonia, then shaken twice with dilute hydrochloric acid, washed with water and dried. The reaction products were distilled twice through a semimicro fractionating column.[20] The volume of liquid ammonia in the deuterofluorobenzene experiments was 25 ml. with the potassium and ammonium chloride reduced to 1.2 and 3.2 g., respectively.

In the short-time reactions (under 10 minutes), rapid quenching was essential. This was achieved by forcing a solution containing one equivalent of ammonium chloride in liquid ammonia into the reaction mixture by air pressure.

Determination of Extent of Deuterium–Protium Exchange.—The infrared spectra of the deuterobenzene derivatives, the non-deuterated compounds and the exchange reaction products were determined with a Perkin–Elmer Model 21 Spectrometer, using a 0.028 mm. sample cell *vs.* a salt block. The major absorption peaks appearing in the spectra of the deuterated compounds which were not found in the spectra of the non-deuterated substances, together with their molecular extinction coefficients, are given in Table II.

For each deuterium derivative, absorption peaks of moderate intensity in a region relatively free of absorption by the corresponding non-deuterated derivative were chosen. In addition to the absorption of the pure deuterium compound measurements were made on solutions containing 25, 50 and 75 mole % of non-deuterated substance. The absorption intensity for each of the analytical peaks was determined by the method of Heigl, Bell and White.[21] A linear least-square fit was made to the absorption intensity and concentration data. The resulting calibration plot was used to calculate the composition of the reaction products from the intensity of the characteristic infrared absorption peaks. The results are given in Table I.

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[19] M. J. Schlatter, *Org. Syntheses*, **23**, 20 (1943).

[20] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[21] J. J. Heigl, M. F. Bell and J. U. White, *ibid.*, **19**, 293 (1947).

PASADENA 4, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES]

Application of the Hammett Equation to the Substituted Tetrazane–Hydrazyl Free Radical System. I. Equilibrium Constants[1]

BY W. K. WILMARTH AND NEWTON SCHWARTZ

RECEIVED MARCH 18, 1955

The equilibrium constants for the dissociation of the substituted 1,1,4,4-tetraphenyl-2,3-dibenzoyltetrazanes (where the phenyl substituents are *para* CH_3, H and Br) to form the 1,1-diphenyl-2-benzoylhydrazyl free radicals have been determined in acetone. The equilibrium constants can be correlated with the Hammett ρ–σ equation with a ρ of -1.52. A linear relation exists between entropies and enthalpies, and this is discussed in reference to the Hammett equation with the conclusion that differences in enthalpies reflect relative potential energies. The effect of substituents is interpreted in terms of the radical resonance energies, which are determined by the formation of a three-electron bond. It was found that the nitro substituted radicals form complexes with the nitro substituted 1,1-diphenyl-2-benzoylhydrazines.

Introduction

The Hammett ρ–σ equation,[2a] which correlates the effects of *meta* and *para* substituents on rate and equilibrium constants for aromatic systems, was originally established and has had its most frequent applications in the field of heteropolar reactions. In recent years,[3] the equation has been applied with a fair degree of success to the kinetic data of a variety of reactions involving the formation or reactions of free radicals. The applications of the equation to the unimolecular dissociation of a homopolar bond to form two free radicals are interesting because of the implication of the nature of the forces which affect the strength of that particular bond.[4] However, the prototype of such a reaction, the dissociation equilibria of substituted hexaphenylethanes, is generally recognized as not being correlatable with the Hammett equation, since substituents with either positive or negative σ-values increase the dissociation.[5]

Since all the applications of the Hammett equation to free radical systems involve the calculation of rate constants or reactivity ratios, and in view

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[1] A portion of this work was presented at the 126th Meeting of the American Chemical Society, New York, September, 1954. Based on the Dissertation presented by Newton Schwartz to the Graduate School of the University of Southern California in partial fulfillment for the Ph.D. degree.

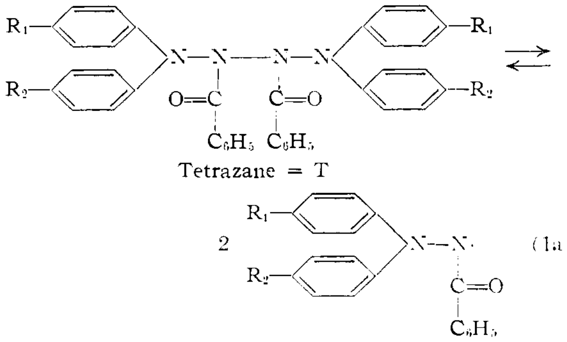
[2] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, (a) p. 184, (b) p. 76.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953), has a complete compilation of applications of the Hammett equation.

[4] (a) C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950); (b) A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951); (c) A. T. Blomquist and I. A. Bernstein, *ibid.*, **73**, 5546 (1951).

[5] C. S. Marvel, C. M. Himel and J. F. Kaplan, *ibid.*, **63**, 1892 (1941); C. S. Marvel, F. C. Dietz and C. M. Himel, *J. Org. Chem.*, **7**, 392 (1942); C. S. Marvel, J. Whitson and H. W. Johnston, THIS JOURNAL, **66**, 415 (1944).

of the discrepant hexaarylethane system, a correlation of equilibrium dissociation constants in even a single instance would greatly strengthen the probability that the equation was of general validity. In a previous note[6a] it was demonstrated that the data of Goldschmidt and Bader[6b] on the dissociation of the substituted tetrazanes (equation 1) showed such a correlation with the conventional σ-values, but the conclusion was only tentative because of the approximate corrections necessary for different solvents and temperatures. Therefore the equilibrium dissociation constants, K, and the associated thermodynamic quantities have been determined in acetone for the tetrazane system.


Tetrazane = T

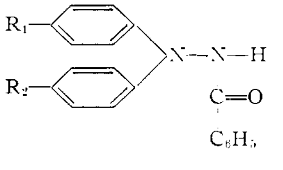
(1a)

Hydrazyl = M

$$K = [M]^2/[T] \qquad (1b)$$

Experimental Procedures

Preparation of the Compounds. The Substituted 1,1-**Diphenyl-2-benzoylhydrazines.**—The compounds have the structure as shown below in which R_1 and R_2 were CH_3, H, Br and NO_2 and were prepared by the Tafel-Gattermann reaction as reported by Goldschmidt and Bader.[6b]


(2)

The yields of the mono- and dinitro substituted hydrazines after purification were only 5–10%. These nitro compounds can be prepared in 30–60% yields by an adaptation of the method for synthesizing diphenylamines.[7] When equimolar amounts of 1-[4-nitrophenyl]-2-benzoylhydrazine, 4-bromonitrobenzene or bromobenzene, and potassium carbonate are refluxed in diethyl carbitol (b.p. 185°) with approximately 0.05 g. each of finely divided copper, cuprous iodide and iodine for a period of 12 to 18 hours with vigorous stirring, the compounds can be isolated by steam distillation of all volatile material followed by crystallization of the residue from acetic acid. The compounds prepared in this way are identical in melting points, analyses, and absorption spectra to those of the Tafel–Gattermann reaction. This method is not general since only tars were obtained when an attempt was made to synthesize 1,1-bis-(*p*-tolyl)-2-benzoylhydrazine.

The previous workers reported that 1,1-diphenyl-2-benzoylhydrazine when oxidized to the radical with potassium ferricyanide in an alcohol–water medium gave a mixture of red and blue solids, but stated that the blue color quickly disappeared.[6] A violet color, presumably a mixture of blue and red, also was reported when the same compound, though synthesized by a completely different method, was oxidized with sodium hypochlorite in ethanol.[8] We have found that the material responsible for the blue color is a colorless oxidizable impurity in the original 1,1-diphenyl-2-benzoylhydrazine. It was separated from the bulk of the hydrazine by chromatography from toluene on acid-washed alumina, whereupon a light blue band appeared. The blue color seemed to result from partial decomposition of the impurity.

The impurity is a white compound (m.p. 250–253°), with an empirical formula of either $C_{25}H_{21}N_2O_3$ or $C_{25}H_{21}N_2O_2$. It turns blue if exposed to light but is quite stable in the dark. The compound can be oxidized with lead dioxide in acetone or toluene below 0° to give relatively stable pure blue solutions. These blue solutions have the properties of radicals in that they react with hydrazobenzene or nitric oxide instantaneously at low temperatures to destroy the blue color. In the case of hydrazobenzene, the blue color reappears on warming, presumably indicating a relatively slow equilibrium between a colorless dimer and the colored radical.

The purified 1,1-diphenyl-2-benzoylhydrazine gave the correct analysis for the desired compound, and oxidation resulted in only a pure red color. A similar impurity was found in the monobromo substituted hydrazine. Table I gives the physical properties of the purified hydrazines, and the spectra of all the radical solutions derived from these purified compounds show only one absorption peak in the visible wave lengths with no apparent shoulders. The analysis for the dibromo compound is the last of several which were performed after different purifications, which included many crystallizations from toluene and ethanol as well as chromatography. The analysis indicates that there is an impurity present, but it must be such that it does not show up in the ultraviolet absorption spectrum of the hydrazine or in the visible absorption spectrum of the radical derived from the hydrazine. It is believed that it must have chemical and physical properties which could not affect subsequent measurements in the small amount that was present. The dinitro compound partially decomposes at temperatures above 230° and the melting point listed was the highest observed when the sample was inserted at 280°.

The Radical Solutions.—The radicals were derived from the compounds listed above by oxidation with lead dioxide. Normal methods of synthesis were used, since these radicals do not react with oxygen. They do decompose at an appreciable rate at room temperature, so that the preparation and physical measurements must be made at well below 0°. Moreover, the radicals are extremely reactive toward acids, the latter immediately decolorizing the solutions.

Generally, two to three millimoles of the substituted hydrazine were dissolved in 200–300 cc. of solvent at room temperature, or higher, in a three-necked flask with a very efficient stirrer, and 10–20 g. of potassium carbonate added. The flask then was immersed in a Dry Ice-bath, and when the temperature reached 0°, 20–40 g. of freshly precipitated lead dioxide[9] was added, and within 30 seconds the solution was cooled to −30°. This procedure usually gave a 60–95% yield of radical, but when it did not, the solution was quickly warmed to 0° and recooled. The solution was filtered through a medium sintered glass Büchner funnel which had a receiver below and a ground joint on top, so that it could be closed completely during filtration, as well as an outer jacket which could be filled with solvent and maintained at the temperature desired with the use of Dry Ice The yields in toluene and methylene chloride were 75–95%, but in acetone the oxidation was much slower, resulting in yields of 10–30%. When higher concentrations were required in acetone, the sample was oxidized in methylene chloride and, after filtration, the methylene chloride was removed completely by vacuum distillation at −30 to −60° in a period of two hours, and the residue dissolved in acetone. Even with this procedure, along with the addi-

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(6) (a) N. Schwartz and W. K. Wilmarth, *J. Chem. Phys.*, **20**, 748 (1952); (b) S. Goldschmidt and J. Bader, *Ann.*, **473**, 137 (1929).

(7) I. Goldberg, *Ber.*, **40**, 4541 (1907).

(8) R. Stolle and W. Reichert, *J. prakt. Chem.*, [2] **122**, 348 (1929).

(9) Commercial lead dioxide gave only a 3–5% yield of radical on shaking for 24 hours at −20 to 0°. The lead dioxide was prepared by dissolving 75 g. of lead tetraacetate in 200 cc. of glacial acetic acid and 20 cc. of $CHCl_3$ in a water-bath, and adding 20 cc. of water. The lead dioxide was separated by centrifugation, washed six times with 200 cc. of acetone, and once with the solvent in which it was to be used. R. Kuhn and I. Hammer, *Ber.*, **83**, 413 (1950), reported an "active" preparation but their material is not as active as that reported here, although more efficient than the commercial product.

TABLE I

ANALYSES AND MELTING POINTS OF THE SUBSTITUTED 1,1-DIPHENYL-2-BENZOYLHYDRAZINES

		Analyses, %								M.p., °C.	
		Found				Calculated					
R_1	R_2	C	H	N	Br	C	H	N	Br	Found	Lit.[a]
CH_3	CH_3	79.86	6.05	8.42		79.71	6.37	8.86		188–189	187
CH_3	H	79.65	6.07	9.09		79.40	6.00	9.26		173–174	172
H	H	79.30	5.42	9.59		79.13	5.59	9.72		190.5–191.5	189
Br	H	63.83	4.17	7.54	21.60	62.13	4.12	7.63	21.80	200–201.5	199
Br	Br	51.72	3.87	5.70	38.10	51.10	3.14	6.28	35.80	235–236	235
NO_2	H	68.05	4.70	12.45		68.40	4.51	12.61		177–178	173
NO_2	NO_2	60.62	3.70	14.61		60.30	3.72	14.80		282–283.5 d	276

[a] Literature melting points are taken from reference 6.

tion of the lead dioxide at room temperature, the yields of the nitro compounds were only 50 to 60%.[10]

Solutions of the radicals are stable at −78° for at least a week, and for the nitro substituted compounds for approximately two months. The exception is the tetratolyl compound which was found to be appreciably decomposed after two days. The equilibrium constant determinations, along with the analysis of this compound, were performed in a period of 36 hours, and hydrazobenzene titration indicated that no decomposition had occurred during that time. No exceptional precautions, other than covering solutions, were taken to prevent contact with atmospheric moisture, and an effect due to moisture has never been observed.

Solvents.—C.P. toluene was refluxed over sodium for two hours, and distilled from sodium through a 15-plate column, discarding the first and last fifths of distillate (b.p. 108.9–109.0°, uncor.). C.P. acetone was refluxed with 20 g. each of potassium carbonate, potassium permanganate and lead dioxide for two hours, and distilled as above (b.p. 56–56.1°).

Cryostat.—The cryostat was an insulated 5-gallon stainless steel can filled with trichloroethylene which was pumped intermittently through a solenoid valve to coils immersed in a Dry Ice-bath. The solenoid valve was controlled by a platinum resistance thermometer through a modified Wheatstone bridge electronic relay. Temperatures down to −30° were measured with a mercury thermometer, while below −30°, a five junction copper–constantan thermocouple, calibrated with ice and triply distilled mercury, was used.

Equilibrium Measurements.—The equilibrium constants were determined with the use of the Beckman model DU spectrophotometer in the temperature range of −10 to −60°. The cell holder consisted of two square holes, to fit the usual square glass cells, in a metal block surrounded by a cooling jacket through which cryostat liquid was pumped. The entire cell, except for the top, was surrounded by a vacuum jacket with the light beam arranged so that no cooling liquid was in its path. Quartz windows with silicone O-rings were used to hold the vacuum. The temperature variation was ±0.02°, except that there was a 1 to 2° temperature differential between the cell and the cryostat, depending upon the operating temperature. When the cell was used for long periods of time, there was enough heat leak to cause moisture condensation on the outside windows, and a stream of dry air was used to prevent this. A similar holder was used for the cylindrical 10-cm. cells, but here the block was slit longitudinally, so that the top could be removed, the cells inserted, and the top replaced. During any one run, the 10-cm. cells were kept in the holder, solutions were removed with an aspirator and the cells washed several times with acetone. The solvent adhering to the walls of the cell was too small in volume to affect subsequent readings.[11]

The dilutions were performed by pipetting an approximate amount of solution into 50-ml. Pyrex volumetric flasks in the cryostat, and the solvent necessary to fill the volumetric flask was weighed. The difference between this weight and the weight of 50 ml. of acetone, using the density data of the "International Critical Tables,"[12] gave the weight of solution diluted. The solutions were equilibrated in the cryostat, and the equilibrium could be approached from both sides by starting with half the solutions at a higher and the other half at a lower temperature. As a check on possible decomposition during the time required to reach equilibrium, a duplicate determination was made on the most concentrated solution where this time was doubled. Although no light-activated decomposition in the spectrophotometer was ever noted, the possibility of such an error was eliminated in the use of separate solutions.

The solutions were kept in the cryostat in small pipets which had sealed fragile tips and an outer jacket, and were delivered into the cells by breaking the tips against the side. The cryostat liquid carried along in the outer jacket prevented warming of the solutions in the transferring process. The temperature differential between the cell holder and the cryostat, in some cases, caused a small increase of optical density with time because of dissociation of the dimer. This drift was corrected for by extrapolation back to the time when the spectrophotometer cells were filled. In all cases, the over-all correction was less than 3% in optical density.

If T_0 is the initial molal concentration (m) of the dimer at each dilution calculated on the basis of no dissociation, D the optical density of the solution and E_m the molal extinction coefficient of the radical, then with the use of the equilibrium expression and the mass balance equation, equation 3 can be derived. By plotting T_0/D vs. D (Fig. 1) and extrapolating to zero optical density, both the

$$T_0/D = D/(KE_m^2) + 1/(2E_m) \qquad (3)$$

equilibrium constant, K, and the extinction coefficient can be evaluated. The largest error involved in the equilibrium constant is the evaluation of the extinction coefficient, since small changes in the slope give relatively large changes in the intercept. Since the extinction coefficient showed no systematic trend in the small temperature interval used, the average extinction coefficient of all the runs was used to calculate the equilibrium constant from the slopes of the lines.

Analyses of the Radical Solutions.—The T_0 concentrations were determined by the amount of nitric oxide taken up by a solution of the radical plus dimer.[13] When nitric oxide was introduced into a solution, the red color of the radical instantaneously disappeared to give a light yellow colored solution,[14] and a slow absorption followed because of dissociation of the dimer. At the end of the reaction, the solution was cooled to −70°, where the vapor pressure of acetone is 0.3 mm., and the dissolved nitric oxide was distilled into a liquid nitrogen trap. A Dry Ice trap was substituted for the liquid nitrogen and the nitric oxide was pushed back into the burets with a Töpler pump. The difference between initial and final readings gave the total absorption due to radical plus dimer. The weight of the solution was determined by weighing the cell filled and empty at the end of the reaction. Table II gives four analyses performed on the same solution at different temperatures and indicates the reproducibility, as well as the non-occurrence of the complications recently observed with triphenylmethyl and oxygen.[15] Concentrations also were determined

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[10] Potassium carbonate was not used with the nitro compounds, since they form the red potassium salts of the hydrazines.

[11] We are indebted to Mr. B. B. Varnes and Mr. S. W. Bale of the Physics Department Machine Shop for the construction of the low temperature attachments to the Beckman spectrophotometer, as well as for many valuable suggestions concerning its design.

[12] "International Critical Tables," Vol. 3, 1926, p. 28.

[13] W. K. Wilmarth and N. Schwartz, THIS JOURNAL, 77, 4551 (1955).

[14] The decomposition products of the radical have a distinctive brownish-red color. If this color was detected at this point, the solution was not used for the equilibrium determinations, since there is some overlap of radical and decomposition product spectra.

[15] N. N. Lichtin and G. R. Thomas, THIS JOURNAL, 76, 3020 (1954).

by hydrazobenzene titration[6b] and agreed to within ±5% of the method used above.

Table II

Analyses of the Same Solution of 1,4-Diphenyl-1,4-bis-(4-bromophenyl)-2,3-dibenzoyltetrazane at Different Temperatures

Temp., °C.	Nitric oxide absorbed, 0.5 atm. and 25.0°, cc.	Wt. of solvent, g.	$T_0 \times 10^3$, moles/kg.
−15.0	9.24	60.6	1.57
−20.0	9.36	57.9	1.66
−30.0	9.38	60.0	1.60
−40.0[a]	9.81	60.4	1.66
		Av.	1.62 ± 0.04

[a] This run was followed for 90% of the reaction at −40°, and then warmed to −10° to complete the reaction.

Results

The spectra of all the radical solutions contain a single peak in the visible range of 500 to 530 mμ. This peak has been ascribed to the radical since it increases with increasing temperature, and all equilibrium measurements have been performed using optical density readings in this region. Figure 1 gives representative plots of T_0/D against D for the ditolyl substituted dimer for runs at four different temperatures. This plot demonstrates the expected coincidence of the intercepts at the different temperatures. Table III gives the temperature, the range of concentrations, the range of time from the most concentrated to the most dilute solution to attain equilibrium, the molal extinction coefficient, λ_{max}, the wave length of maximum absorption, and the molal equilibrium constant, K_m. Figure 2 gives the plot of log K_m against $1/T$, while Table IV gives the molar equilibrium constants, K_c, at −30.0°, calculated with the use of the density data for acetone from reference 12. The enthalpies were determined from the plot of log K_m against $1/T$, while the entropies were determined from the plot of ΔG_m against T, and these values are shown in columns 6 and 8 of Table IV.

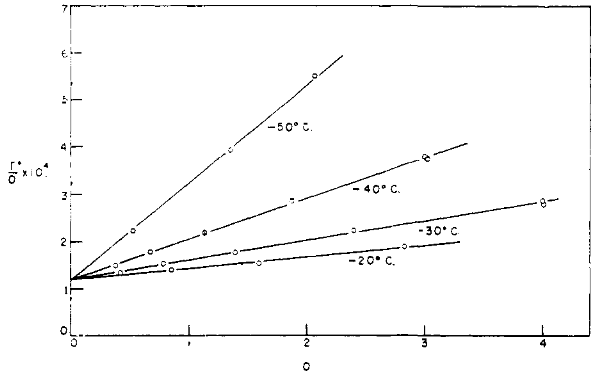

Fig. 1.—Spectrophotometric analysis of dissociation equilibrium constants for 1,4-bis-(p-tolyl)-1,4-diphenyl-2-3-dibenzoyltetrazane in acetone.

Table III

Equilibrium Dissociation Constants for Substituted 1,1,4,4-Tetraphenyl-2,3-dibenzoyltetrazanes in Acetone

R_1	R_2	T, °C.	Range of $T_0 \times 10^4$, moles/kg.	Time, hr.	λ_{max}, mμ	$E_m \times 10^3$	$K_m \times 10^4$, moles/kg.[b]
CH_3	CH_3	−30.0	0.3– 5	1–2	526	4.54	63
		−38.5	.3– 5	2.5–3.5		4.54	38
		−49.6	.3– 5	5–6		4.53	16.8
		−59.1	.3– 5	8–9		4.56	9.4
CH_3	H	−19.6	.6– 5	0.5–1	516	4.24	21.8
		−29.9	.6–11	1–2		4.16	11.4
		−39.0	.6–11	2–3		4.31	6.1
		−49.7	.6–11	4–5		4.67	2.08
H	H	−20.0	.2–24	1–3	508	2.79	9.9
		−29.5	.2–24	2–4		2.84	5.3
		−50.0	.2– 9	4–5		2.82	0.82
Br	H	−19.8	.2–53	0.25–0.5	520	3.21	2.21
		−20.3[a]	.8–18	2.5–3.5		3.27	2.26
		−30.3	2.4–18	2–3		3.13	.98
		−40.1	0.8–18	6–8.5		3.20	.40
		−49.9	.8– 8	7–9		3.06	.156
Br	Br	−10.2	1.0–16	0.25–0.5	526	3.82	1.09
		−20.0	1.0–16	1–2		3.66	0.53
		−30.0	1.0–16	3–4		3.70	.198
		−39.5	1.0–16	4–5		3.57	.076

[a] The concentration of the original solution for this and the following three runs was determined by hydrazobenzene titration, since at the end of the nitric oxide analysis it was found that carbon dioxide, which is absorbed slowly by all the solutions, had not been removed completely in the degassing procedure. [b] The error in K_m is approximately ±5%.

The successful correlation of the equilibrium constants with the Hammett equation is shown in Fig. 3, where the factor 2 is included in the sum of the σ-values for the abscissas to account for the symmetry of substitution in the tetrazane molecule.[16] In the same figure are listed the ρ-value, s the standard deviation, r the correlation coefficient and (log K^0)$_{calcd}$ which were all evaluated according to Jaffé.[2]

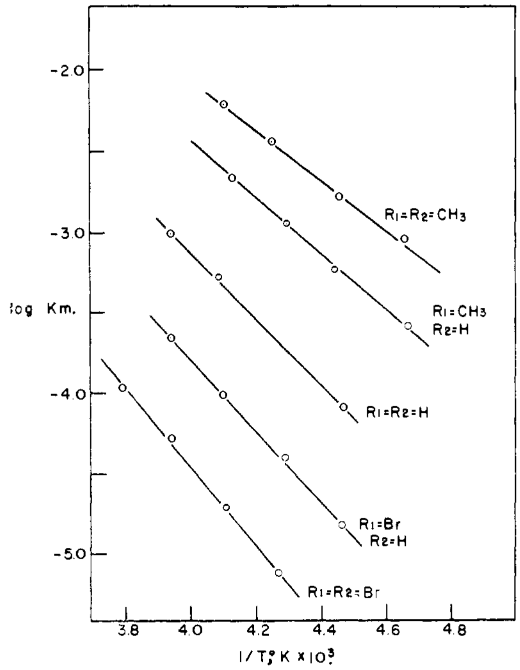

Fig. 2.—Temperature coefficient plot for the molal equilibrium constants in acetone.

The ρ–σ plot occurs despite non-constant entropy values, but these quantities are linearly related to

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(16) In the original note[6a] the σ-values are too small by the same factor of 2, so that the ρ-value of −2.6 should be corrected to −1.3.

TABLE IV

THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION EQUILIBRIUM OF THE SUBSTITUTED 1,1,4,4-TETRAPHENYL-2,3-DIBENZOYLTETRAZANES IN ACETONE AT −30.00°

R_1	R_2	$2(\sigma_1 + \sigma_2)$	$K_c \times 10^4$, moles/liter	ΔG^0,[a] kcal./mole	ΔH^0,[a] kcal./mole Exptl.	Calcd.	ΔS^0, e.u. Exptl.	Calcd.
CH_3	CH_3	−0.680	53.6	2.42	6.7	6.8	18.0	18.0
CH_3	H	− .340	9.46	3.35	7.9	7.8	19.6	19.6
H	H	.000	4.15	3.75	9.2	8.9	23.9	21.1
Br	H	+ .464	0.625	4.62	10.9	10.3	23.2	23.1
Br	Br	+ .928	0.170	5.29	11.2	11.8	25.1	25.1

[a] The error in the enthalpy values is ±0.5 kcal. and in the entropy values about ±2 e.u., when these are listed under columns headed (exptl.). $\Delta H^\circ - T\Delta S^\circ$ does not necessarily equal ΔG°, since the former represents the average over-all temperatures, while ΔG° is evaluated only from one temperature.

the enthalpy values[3b,c,17] (Table IV). Equation 4 gives the quantitative relationship between the entropies and enthalpies, where the thermodynamic quantities represent the difference between any substituted compound and the parent compound in

$$T\Delta\Delta S^0 = 0.32\Delta\Delta H^0 \tag{4}$$

kcal./mole and T is 243°K. Thus the entropies compensate for the enthalpy changes by approximately 30% at this temperature. The entropies and enthalpies are both linear with σ [where σ is equal to $2(\sigma_1 + \sigma_2)$] as shown by equations 5a and b, which were evaluated from graphical plots. Calculated values using these equations are shown in Table IV (columns 7 and 9), indicating that these equations do not distort the data beyond the experimental error. A similar dependence has been observed for both the dissociation and recombination rate constants, where the entropies also compensate for the enthalpy changes by 30%.[13]

$$\Delta H^0 = 3.2\sigma + 8.9 \tag{5a}$$
$$\Delta S^0 = 4.3\sigma + 21.2 \tag{5b}$$

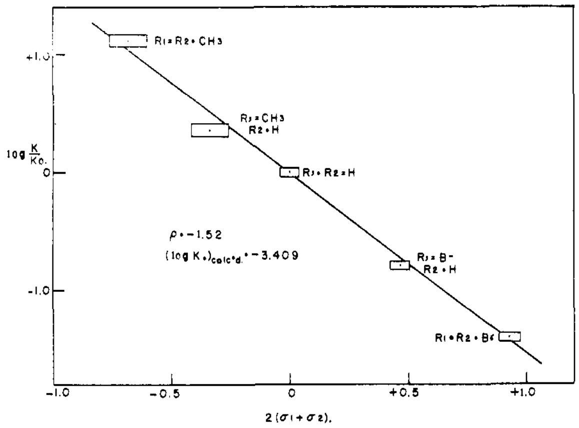

Fig. 3.—ρ–σ plot for dissociation equilibrium constants in acetone at −30.00° s = 0.13 and r = 0.994.

Measurements on the Nitro Substituted Compounds.—Ten-cm. cells were used to measure the optical densities of solutions of the nitro substituted compounds since the absorption in the region of 500–600 mμ is very small at −30 to −20° and considerable decomposition occurs at higher temperatures. For the 1,4-diphenyl-1,4-bis-(4-nitrophenyl)-2,3-dibenzoyltetrazane solutions, the results gave a large scatter of points on the usual plot of T_0/D against D, and the intercepts for different temperatures were far apart. This anomalous behavior can be traced to the presence of unoxidized 1-phenyl-1-(4-nitrophenyl)-2-benzoylhydrazine[18] in the solution. Figure 4 shows the spectra of solutions containing a fixed amount of dimer but with various amounts of added hydrazine. The large increase below 490 mμ is due to the spectrum of the hydrazine itself (the dotted line is the spectrum of a solution of MH_0 alone). However, above 510 mμ, where the hydrazine shows no absorption, the optical densities increase with increased MH_0 concentration. When the contribution from MH_0 below 510 mμ is subtracted, the resulting curves show a maximum in absorption. However, the wave length of maximum absorption of 490 mμ for the lowest concentration gradually shifts to 500 mμ for the highest, indicating that the correction is not too accurate. If readings are confined to above 530 mμ the complication of MH_e absorption can be avoided. Figure 5 shows the optical densities at different wave lengths of solutions of constant T_0 concentration, but with varying MH_0 concentration, while Fig. 6 shows the same for a constant MH_0 concentration and varying T_0 concentration. These results indicate that the increase in optical density is proportional to the first power of the concentration of MH_0 and to the square root of the T_0 concentration. Addition of MH_0, furthermore, does not increase the T_0 concentrations of the solutions so that there is nothing in solution which is oxidizing the added hydrazine to the radical.

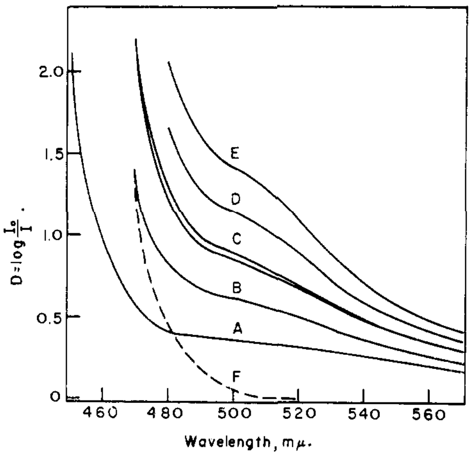

Fig. 4.—Absorption spectra of acetone solutions of the dinitro substituted tetrazane at −30.0°, 10-cm. light path: A, $T_0 = 4 \times 10^{-4}\ m$, $MH_0 = 1.4 \times 10^{-3}$, MH_0 concentration based on oxidation yield; B, $T_0 = 4 \times 10^{-4}\ m$, $MH_0 = 4.0 \times 10^{-3}\ m$; C, $T_0 = 4 \times 10^{-4}\ m$, $MH_0 = 8.5 \times 10^{-3}\ m$, the two curves represent approach to equilibrium from high and low temperatures; D, $T_0 = 4 \times 10^{-4}\ m$, $MH_0 = 12.0 \times 10^{-3}\ m$; E, $T_0 = 4 \times 10^{-4}\ m$, $MH_0 = 15.8 \times 10^{-3}\ m$; F, pure $MH_0 = 7.34 \times 10^{-3}\ m$.

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(17) C. G. Overberger and R. W. Cummins, THIS JOURNAL, **75**, 4250 (1953).

(18) In this section, MH_0 will represent the amount of hydrazine present in the solution before any interaction, while MH_e will represent the amount at equilibrium. T_0 and T_e have the same significance with respect to the dimer.

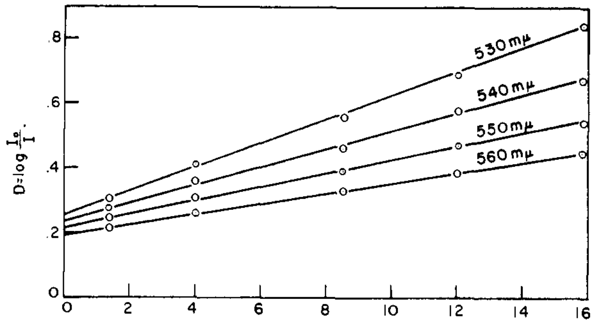

Fig. 5.—Variation of optical densities of acetone solutions of the dinitro substituted tetrazane at −30° with MH_0 concentration; T_0 constant at 4 × 10^{-4} *m*, 10-cm. light path.

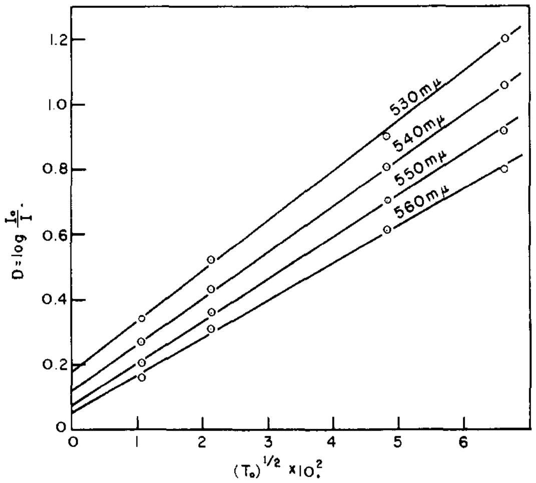

Fig. 6.—Variation of optical densities of acetone solutions of the dinitro substituted tetrazane at −30° with the square root of T_0 concentration; MH_0 constant at 7.5 × 10^{-3} *m*, 10-cm. light path.

Considering that the reddish color of the solutions is immediately removed in the presence of hydrazobenzene or nitric oxide, and that the observed rates of dissociation are independent of MH_0 concentration[13] these results are all consistent with a colored complex formed from the radical and unoxidized hydrazine. Analysis of the system on this basis predicts that plots such as Figs. 5 and 6 should have a zero intercept independent of the wave length. The positive intercept implies another species which also absorbs in this region. However, no consistent treatment is arrived at by postulating the following pairs with overlapping spectra: (a) monomer and complex, (b) dimer and complex. Although it seems evident that a complex does exist, there must be some other perturbing factor which has not been evaluated. Since the readings are at low optical density, small amounts of decomposition products could be responsible.

Although this system cannot be treated quantitatively, some estimate of the association constant to form the complex can be made. From the variation of optical density of the solution with MH_0 concentration, and on the assumption that $T_e = T_0$ and $MH_e = MH_0$, the equilibrium constants are shown for the two equilibria in equation 6 where C represents the concentration and E_c the extinction coefficient of the complex, and M the concentration of the radical. The K_r is based on a prediction of the dissociation equilibrium constant from the

$$1/2T + MH \rightleftarrows C$$

$$K_c = \frac{0.6 \pm 0.3 \times 10^3}{E_c} \cong 0.2 \qquad (6a)$$

$$M + MH \rightleftarrows C$$

$$K_r = \frac{0.2 \pm 0.1 \times 10^7}{E_c} \cong 6 \times 10^2 \qquad (6b)$$

ρ–σ plot. Since the color of the complex probably would be due essentially to the radical, E_c is probably of the same order of magnitude as the extinction coefficients listed in Table III, approximately 3 × 10^3. These constants are minimum estimates, since smaller coefficients would give correspondingly larger association constants.

The usual plots of T_0/D against D for the tetranitro compound show the same behavior as above, but addition of MH_0 causes no change in the spectrum beyond that expected for MH_0 itself. An increased association constant could account for this since the yields on oxidation had never been greater than 50%. Because of the complications demonstrated by these compounds, equilibrium constants for the dissociation to radicals could not be evaluated. This effect was not noticed by Goldschmidt and Bader[6b] since they made a single determination at only one concentration.

Discussion

Linear Entropy–Enthalpy Relations and the Hammett Equation.—An analysis of the effects of enthalpy and entropy on the free energy changes is a necessary precedence to an interpretation of the results. Hammett has[2] added to his original criterion that the ρ–σ equation is successful only when $\Delta\Delta S = 0$, and has concluded that if $\Delta\Delta S$ is linearly dependent on the enthalpy it may be incorporated in the latter. This result is demonstrated in equation 7 and shows that under these special conditions, as in the case where $\Delta\Delta S = 0$, the correlation is a function of enthalpy changes alone. The thermodynamic quantities $\Delta\Delta G_i$,

$$\log K/K^0 = -\Delta\Delta G_i/2.3RT$$
$$= -(\Delta\Delta H_i - T\Delta\Delta S_i)/2.3RT \qquad (7a)$$

but

$$T\Delta\Delta S_i = \alpha\Delta\Delta H_i \qquad (7b)$$

then

$$\log K/K^0 = -\Delta\Delta H_i(1 - \alpha)/2.3RT \qquad (7c)$$

$\Delta\Delta H_i$ and $\Delta\Delta S_i$ are differences between any substituted and unsubstituted compound and relate to either rate or equilibrium processes.

The importance of the entropy contribution for systems of this type can be seen by referring to equations 7b and c. The coefficient α increases as the temperature increases if it is assumed that $\Delta\Delta H_i$ and $\Delta\Delta S_i$ are relatively independent of temperature. A "critical" temperature exists at which α is equal to unity. At this temperature, the $T\Delta\Delta S_i$ term completely compensates for the enthalpy, and ρ becomes zero; beyond this temperature ρ changes in sign. The sign of ρ frequently is used to determine whether a reaction is facilitated by high or low electron densities at the reaction site, and it is obvious that such a criterion may be an accident of the choice of temperature. A better criterion, apparently, is the sign of the slope of the plot of $\Delta\Delta H_i$ against σ. The critical temperature, T_c, can be calculated from α and the experimental temperature, T_{exp}, where $T_c = T_{exp}/\alpha$. For the tetrazane system, T_c is equal to 760°K. by using an average of 0.32 for α.[19]

Although such an analysis describes the similarities in systems where the entropy is constant to those where it is linearly dependent on the enthalpy, it does not remove the difficulty that the $\Delta\Delta H_i$ include terms due to kinetic as well as potential energy changes.[1b] It is necessary to know the relative potential energies at absolute zero of temperature to have a true measure of the effect exerted by substituents on the electronic configuration within the molecule. An alternative approach is to evaluate whether the trend of $\Delta\Delta H_i$ with substituents at some temperature of observation is markedly different from that at absolute zero. To understand the increments contributing to $\Delta\Delta H_i$ and $\Delta\Delta S_i$ at some temperature T (called $\Delta\Delta H_i^T$ and $\Delta\Delta S_i^T$), a cycle can be considered where radical and dimer, each in their standard states, are cooled in acetone to 0°K. to form solutions of these solvated species in an acetone glass. Assuming that the contributions to the heat capacities below 1°K. are negligible and that heat capacities are constant with temperature, then equation 8 and 9 relate the relative enthalpy and entropy at a temperature T to the same quantities at absolute zero in the acetone–glass solution, where the $\overline{C}_i$ quantities are the partial molar heat capacities of the solutes. All thermodynamic quantities refer to solvated species, and it is assumed that the solvation does not change with temperature. Since it is well known that heat capacities decrease with temperature, $\Delta\Delta\overline{C}_i$ represent the average quantities over the temperature range 0–T, °K.

$$\Delta\Delta H_i^T = \Delta\Delta H_i^0 + T\Delta\Delta\overline{C}_i \qquad (8)$$

$$\Delta\Delta S_i^T = \Delta\Delta S_i^0 + \ln T\ \Delta\Delta\overline{C}_i \qquad (9)$$

There are two extreme cases which can be discussed, depending on whether $\Delta\Delta S_i^0$ is finite or zero. $\Delta\Delta S_i^0$ represent the difference in entropies between crystalline and solvated components at absolute zero. In cases where the $\Delta\Delta\overline{C}_i$ are zero, $\Delta\Delta S_i^0$ and $\Delta\Delta H_i^0$ completely determine $\Delta\Delta S_i^T$ and $\Delta\Delta H_i^T$, and marked differences of solvation as the substituent is changed would relate the relative entropies and enthalpies. There are two important objections to the acceptance of this view. It is empirically known[20] that the solubilities of a particular organic solute in a variety of solvents demonstrate a linear relation between entropies and enthalpies. However, only limited correlation exists for different solutes in the same solvent, a condition that is present in systems to which the Hammett equation applies. This difference in correlation is not surprising since the crystal energy is held constant in the former, while in the latter it varies from solute to solute. The second objection is that this view leads to the prediction that the Hammett equation can be applied to solubility equilibria. Since the coefficients relating the entropies and enthalpies in the present work are approximately the same observed for the solubility correlations,[20] then $\Delta\Delta H_i^T$ and $\Delta\Delta S_i^T$ would be completely solvation dependent. Inspection of equation 7a reveals that the relative free energies would then relate to differences in solubilities between the substituted reactants and products. To test this prediction, the Hammett equation was applied to the solubilities of liquid and gaseous monosubstituted benzenes and crystalline substituted benzoic acids in water,[21] but with no success.

The alternate case is that $\Delta\Delta S_i^0$ would be zero because differences in solvation caused by the change in substituents would cancel when comparing the dimers to two moles of the monomers. Under such circumstances it is possible to estimate $\Delta\Delta\overline{C}_i$ from equation 9 and correct $\Delta\Delta H_i^T$ to absolute zero. For instance, the $\Delta\Delta S^0$ value of 3 cal./°K. for the dimethyl substituted compound and the parent compound would only correct the $\Delta\Delta H^0$ value of 2.5 kcal./mole by less than 0.1 kcal./mole. This correction refers the $\Delta\Delta H_i^T$ to the lowest vibrational quantum state, and since the correction is insignificant with respect to the energy differences at higher vibrational states, it can be assumed that the variations in zero point energies also will be negligible. In this particular case, despite the profound contributions of the entropies to the ρ-value of each plot, it appears that the enthalpies still may be used reliably as a measure of potential energies.

In view of the above discussion, it will be assumed that the difference in solvation energy of dimer and monomer remains relatively constant, and that $\Delta\Delta H_i^T$ primarily represents differences in electronic energy. Testing the assumption would require a study in a variety of solvents to determine whether there is a variation of ρ and $\Delta\Delta H_i^T$ with solvent.

There have been many explanations for linear, entropy–enthalpy relations covering both rate and equilibrium data.[20,22] In recent calculations for bimolecular associations in the gas phase, it was proposed that the vibrational contribution of the new bond in the dimer to the entropy change is a significant criterion of a weak or strong bond,[23] suggesting a possible relationship between vibrational entropies and bond energies. For our series of related compounds the translational and rotational contributions to the entropies are probably quite

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[19] Dr. J. E. Leffler of the Florida State University, in a personal communication to Professor N. K. Kharasch of this Department, has performed a survey, to be published shortly, of systems where entropy and enthalpy are related, and has made the same conclusions as presented here, although in a different form.

[20] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1335 (1936); **33**, 166 (1937); A. Wasserman, *J. Chem. Soc.*, 621, 625 (1942).

[21] A. Seidell and W. F. Linke, "Solubilities of Inorganic and Organic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1952.

[22] (a) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937); (b) U. K. Kochi and G. S. Hammond, THIS JOURNAL, **75**, 3443 (1953); (c) J. Rehner. *J. Polymer Sci.*, **10**, 442 (1953); L. Valentine. *ibid.*, **11**, 382 (1953): (d) R. W. Taft, THIS JOURNAL. **75**, 4534 (1953): (e) H. S. Frank. *J. Chem. Phys.*, **13**, 504 (1945).

[23] A. Shepp, S. H. Bauer, THIS JOURNAL, **76**, 265 (1954); L. Slutsky and S. H. Bauer, *ibid.*, **76**, 270 (1954).

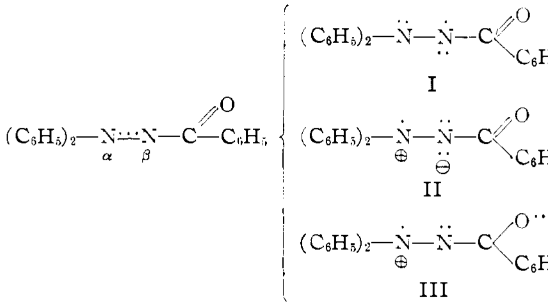
constant, as they are for the substituted acetic acids,[23] so that the $\Delta\Delta S_i$ quantity of equation 7b would represent a measure of differences of vibrational entropies in the dimers.[24] The linear entropy–enthalpy relation thus states that the vibrational movement within a bond decreases as the strength of the bond increases. To include this result in a potential energy diagram, the shape of the wells for the dimers should be broadened at the minimum as the bond energies decrease.

The Effect of Substituents.—The postulate that $\Delta\Delta H_i$ reflect differences in potential energy makes possible an interpretation of the effect of substituents in terms of the resonance energies of the radicals. The first consistent explanation for the stability of the triphenylmethyl analogs was made in terms of the resonance theory,[25] and on this basis an empirical resonance energy for triphenylmethyl of 37 kcal./mole is obtained as half the difference of the dissociation energy of ethane and the dissociation energy of hexaphenylethane. This resonance energy is reduced to approximately 24 kcal./mole if it is corrected for the steric repulsion between the triphenylmethyl groups.[26] This type of calculation ignores compressional energy terms,[27a] but since they cannot be evaluated easily and do not affect the main conclusions presented in the present work, they will be assumed constant in all compounds.

A similar calculation can be performed for the hydrazyl radicals, where the reference N–N bond energy is taken as 60 kcal./mole, the bond energy in hydrazine,[28] since the parent tetrazane molecule does not exist. The empirical resonance energy for the 1,1-diphenyl-2-benzoylhydrazyl radical is thus 25 kcal./mole. This value probably needs little correction for steric effects, since Fisher–Hirschfelder atom models of the dimer show very little hindrance due to the phenyl and benzoyl groups.[29] This is in sharp distinction to hexaphenylethane, where the central C–C bond cannot be formed with the same models.

The source of this large resonance energy, equivalent to the triphenylmethyl resonance, can be explained using the interpretation of the paramagnetic resonance absorption spectrum of the 1,1-diphenyl-2-picrylhydrazyl radical. On the basis of these data it has been concluded that the odd electron in that radical is symmetrically located between the two nitrogen atoms[30a]; it previously had been suggested that this result would be expected if a three-electron bond existed between those atoms.[30b]

If these results are carried over to the present system, then the forms shown in 10 are the possible hybrids contributing to the radical structure, where forms I and II represent the three-electron bond. The three-electron resonance can account for the calculated resonance energy since it has been estimated that this type of bond has a stabilization of approximately one-half that of a normal single bond,[27b,31] or in this instance 30 kcal./mole. Form III has been included to utilize the lone pair of electrons on the β-nitrogen atom for the amide resonance without disturbing the three-electron resonance.



(10)

The success of the Hammett equation for the tetrazanes is in marked contrast to the hexaphenylethanes. It has been suggested[3a,32] that the latter behavior arises from the added resonance forms provided by the interaction of the odd electron with both negative and positive σ-substituents. The results in the present system are in accord with the paramagnetic resonance data in that they also indicate by inference that the odd electron is localized between the two nitrogen atoms and does not enter the aromatic rings.

Resonance theory does not seem to provide a very satisfactory explanation for the difference in behavior of the two radical systems. A more satis-

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[24] The comparison of the entropy changes in solution to those in the gas phase can be justified on the basis of Trouton's rule. The entropy of dissociation for the acetic acid dimer in the gas phase is 30 e.u. for a standard state of one mole per liter, while in benzene solution, for the same standard state, the value is 20 e.u. [A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 116]. This latter value is quite similar to the entropies of dissociation of the tetrazanes as well as the hexaarylethanes [W. Byerley, H. G. Cutforth and P. W. Selwood, This Journal, **70**, 1142 (1948)]. To use the Trouton rule constant of 15 e.u. for acetic acid it must first be decreased by 4 e.u. to account for the change in standard state in both the gas and solution phase. The assumption that this corrected constant can be applied to both the monomer and dimer of acetic acid leads to a calculated entropy change in solution of 19 e.u. Since the entropy increase in the gas phase is a result of converting vibrational degrees of freedom in the dimer to translational and rotational degrees of freedom in the separated monomers,[23] it appears that the major contribution in solution must be a similar conversion.

[25] L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[26] H. E. Bent and G. R. Cuthbertson, This Journal, **58**, 170 (1936).

[27] C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952: (a) p. 236, (b) p. 151, (c) p. 89.

[28] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950); L. G. Cole and E. G. Gilbert, This Journal, **73**, 5423 (1951).

[29] It is assumed that the dimer is bonded through a N–N bond, although there is no concrete evidence on this point. An alternate structure is one joined through oxygen atoms, as in $(C_6H_5)_2NN{=}C(C_6H_5)O{-}O(C_6H_5)C{=}NN(C_6H_5)_2$. Since C=O and N–N bonds are generally stronger than C=N and O-O bonds, a dimer joined through nitrogen atoms is preferred. Since the odd electron in the radical is localized between the two nitrogen atoms (see later discussion), it would probably take more energy to move it to the oxygen atom before the bond could be formed. If both dimer forms coexist at equilibrium with the monomers, then the observed equilibrium constant would be $K_NK_O/(K_N + K_O)$ where K_N and K_O are the respective equilibrium constants of the radicals with the nitrogen bonded and oxygen bonded dimers. The rates of dissociation would be the sum of two first-order rates. A non-linear log plot would be expected arising from the difference in activation energies required to break an O-O bond compared to a N-N bond. A non-linear log plot never has been observed.[13]

[30] (a) C. A. Hutchison, R. G. Pastor and A. G. Kowalsky, *J. Chem. Phys.*, **20**, 534 (1952); (b) C. H. Townes and J. Turkevich, *Phys. Rev.*, **77**, 148 (1950); (c) H. S. Jarrett, *J. Chem. Phys.*, **21**, 761 (1953).

[31] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 264.

[32] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.

factory approach possibly may be achieved by utilizing the molecular orbital description developed for the two related free radicals, nitric oxide[27b] and diphenylnitric oxide.[33a] Two of the three electrons on the nitrogen atoms can be placed in a low energy *bonding* π-orbital which can conjugate with the benzene rings while the remaining electron would occupy a high energy *antibonding* π-orbital. Finally it must be assumed that the odd electron cannot conjugate effectively with the rings. The nodal plane which exists in an antibonding orbital, or symmetry requirements,[27a] may make it impossible to form an extended delocalized molecular orbital which would include the odd electron.

The interpretation of the effects of the substituents is possible in the resonance picture by using forms I and II. The assumption that the odd electron does not interact with the substituents leads to the conclusion that the substituents exert their normal inductive and mesomeric effects through the rings. Electron-donating substituents would stabilize the charged form of the three-electron resonance by reducing the partial *positive* charge in the α-nitrogen atom.[34] It would be expected that electron-withdrawing substituents would be favorable on the β-nitrogen atom since these would reduce the partial *negative* charge. This is confirmed partially by the data on the 1,1-diphenyl-2-arylhydrazyl system where electron-withdrawing substituents on that atom do increase the dissociation.[35] A molecular orbital description of the effects of substituents in this system has been given previously by Dewar.[33a,b]

It has been proposed recently that the negative ρ-value for the benzoyl peroxide dissociation arises from the electrostatic repulsion of the negatively charged oxygen atoms which link the two benzoyl groups.[3a] By contrast electrostatic repulsion between the two β-nitrogen atoms in the tetrazane dimer must be of minor importance since the ρ-value characterizing substitution at the β-position is presumably opposite in sign to that of the α-position, whereas the same sign would be expected if electrostatic repulsion were the important factor in the dissociation.

Criteria that have been proposed[3a,36] for the successful correlation of a particular free radical system with the Hammett equation may be summarized as follows: (1) that there be no direct resonance interaction of the odd electron with the substituent, and (2) that a polar or ionic process be involved in going to a transition state or product molecules. For the tetrazane system, these criteria are satisfied, respectively, by the insulating properties of the three-electron bond and the formation of the charged form of that same bond.

Acknowledgment.—This work was greatly facilitated by a grant from the Research Corporation.

[33] (a) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 247; (b) THIS JOURNAL, **74**, 3353 (1952).

[34] The explanation that substituents can affect the three-electron bond is consistent with the paramagnetic absorption data[30c] where it has been shown that minor changes in structure in the 1,1-diphenyl-2-picrylhydrazyl radical can distort the symmetry of position of the odd electron.

[35] S. Goldschmidt, *Ber.*, **53B**, 44 (1920); S. Goldschmidt and K. Renn, *ibid.*, **55B**, 628 (1922); S. Goldschmidt. A. Wolff, E. Wolffhardt, I. Drimmer and S. Nathan, *Ann.*, **437**, 194 (1924).

[36] F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES]

Application of the Hammett Equation to the Substituted Tetrazane–Hydrazyl Radical System. II. Dissociation and Recombination Rate Constants[1]

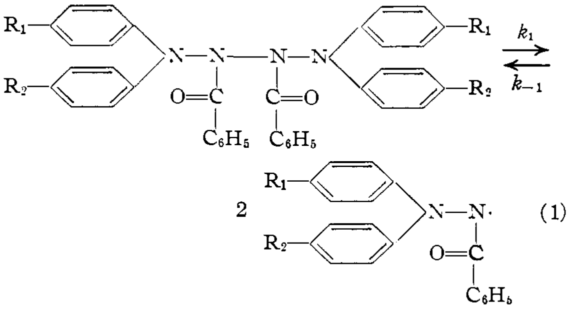
BY W. K. WILMARTH AND NEWTON SCHWARTZ

RECEIVED MARCH 18, 1955

The rates of dissociation of the substituted 1,1,4,4-tetraphenyl-2,3-dibenzoyltetrazanes (where the phenyl substituents are *para* CH_3, H, Br and NO_2) to form 1,1-diphenyl-2-benzoylhydrazyl free radicals have been determined in acetone, and the rates of recombination of the hydrazyl radicals have been calculated from the knowledge of the equilibrium constants. Both rate constants can be correlated with the Hammett ρ-σ equation with the ρ-values of -0.55 and $+0.97$, respectively, for the dissociation and recombination. The effect of substituents is interpreted in terms of the transition state resonance energies arising from the incipient formation of three-electron bonds. A recombination activation energy exists which is dependent on the substituent, and is believed to be associated with the three-electron resonance, although a solvation effect cannot be excluded.

Introduction

In order to determine whether the successful correlation of the equilibrium constants for the tetrazane system[2] with the Hammett equation implies a necessary linear free energy relationship with respect to the rate constants, the rates of dissociation of the substituted tetrazanes (equation 1) have been determined. A knowledge of the equilibrium and rate constants for dissociation makes possible a calculation of the recombination rate constants.



(1)

[1] A portion of this work was presented at the 126th Meeting of the American Chemical Society, New York, September, 1954, Organic Division. Based on the Dissertation presented by Newton Schwartz to the Graduate School of the University of Southern California in partial fulfillment for the Ph.D. degree.

[2] W. K. Wilmarth and N. Schwartz, THIS JOURNAL, **77**, 4543 (1955).