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.

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[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).

LOS ANGELES 7, CALIFORNIA

[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]

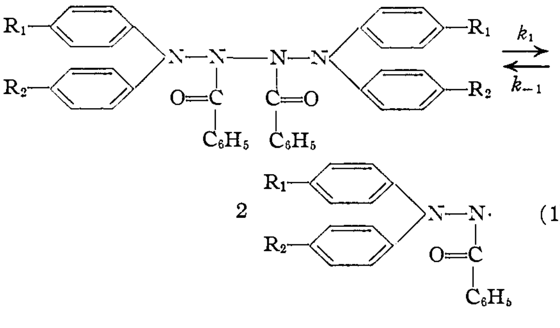
BY W. K. WILMARTH AND NEWTON SCHWARTZ

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)

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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, 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).

These data provide a set of heats and entropies of dissociation, as well as energies and entropies of activation for dissociation and recombination for a particular dimer-free radical system as a function of substituents which cannot affect the steric requirements of the bond that is ruptured.

Experimental

The preparation of the radical solutions, the purification of solvents and the cryostat have been described previously.[2]

Rate Measurements.—The rates of dissociation of the tetrazanes were followed by the Ziegler[3] method using nitric oxide gas at constant pressure. A vacuum line was used containing burets maintained at 25°, a manometer, a Töpler pump and storage bulbs. An automatic pressure regulating device utilizing compressed air raised the mercury in the burets as the absorption proceeded, and volumes of gas could be determined to ±0.02 cc. The reaction vessel was the same as previously reported,[4] except that a small joint was added below the stopcock so that the cell could be filled quickly without decomposition of the solution. After filling, it was closed with a solid plug.

Nitric oxide was taken from a Matheson tank (99% stated purity), but was found to have approximately 20% nitrogen, and the gas readily attacked mercury. It therefore was purified by the method of Giauque and Johnston,[5] except that the distillations were performed at 160–300 mm. in ordinary U-tubes. The nitric oxide after purification had a triple point pressure of 157 mm., which did not increase on further distillation,[5] and no reaction with mercury has ever been observed. The gas was stored in a bulb with a Stock mercury float valve, since Apiezon grease is attacked over a period of months.

Generally, 80 cc. of radical solution was pipetted into the cell with liquid at −70° being pumped through the jacket. The solution was degassed by pumping until the pressure was below 1 mm., 0.5 atm. of hydrogen introduced, and the degassing repeated. The solution then was warmed to the operating temperature for at least 15 minutes, and at zero time nitric oxide was introduced. The red color of the radicals immediately disappeared, and within one minute the solutions were saturated with nitric oxide, so that readings could be taken of the relatively slow absorption that followed. The reactions generally were followed for ten half-lives, and the rate constants were evaluated by plotting log ($CC_t - CC_\infty$) against time, where CC_t is the buret reading at time t, and CC_∞ is the buret reading at infinite time. Figure 1 shows some representative plots. If the time to complete the reaction was inconveniently long, after two or three half-lives the solutions were warmed until the reaction was complete, and then recooled to the operating temperature to determine CC_∞. All such derived rate constants were checked by the Guggenheim method[6] and agreed to within 5%. The rate constants at −30° of both nitro compounds are too small to be determined conveniently by any of the above methods. They were evaluated from the first-order differential equation by following the initial rate of absorption of one cc. of gas at −30° and dividing this rate by the total cc. of gas absorbed at a higher temperature.

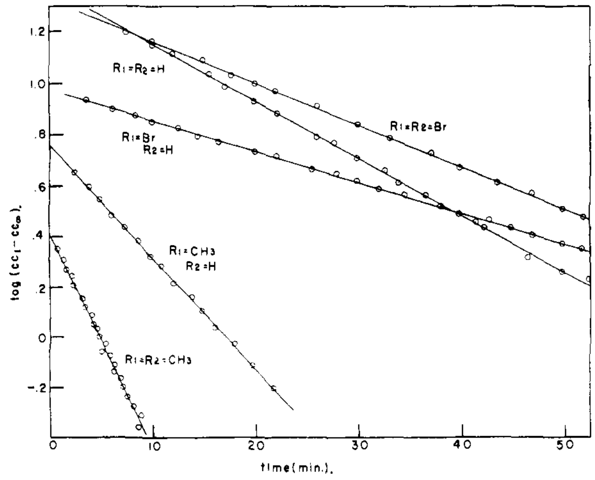

Fig. 1.—First-order log plots for acetone solutions of the substituted tetrazanes at −30°.

Product of the Reaction with Nitric Oxide.—The expected product is an N-nitroso compound, but all attempts to isolate it with the unsubstituted compound led to decomposition. If the product was formed at −30° in toluene, a light yellow solid precipitated from the yellow solution when cooled to −78°, but the solid immediately decomposed at room temperature to give red tars.

If the solutions were warmed to room temperature after the nitric oxide had been removed, the red color of the radical reappeared at a visually observed rate which was much slower than that expected from the dissociation rate constant of the dimer. If nitric oxide was left in the solution for 24 hours at room temperature, the red color did not reappear, and approximately 1 to 1.5 moles of nitric oxide were absorbed per initial mole absorbed in the quantitative reaction at −30°, while one mole of nitrogen was given off. These facts indicate that the decomposition of the products is quite complicated, but this is not surprising considering the well known instability of the N-nitrosoanilides.[7] This process did not affect the rate measurements since nitrogen never was observed at the end of any run.

Results

Dissociation Rate Constants.—The dissociation of the tetrazanes to hydrazyl radicals, and the reaction of the radicals with nitric oxide can be formulated as in equation 2, where T represents the dimer, M the monomer, and P the product of the reaction with nitric oxide.

$$\mathrm{T} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M} \qquad \mathrm{M} + \mathrm{NO} \xrightarrow{k_2} \mathrm{P} \qquad (2)$$

If the second step is extremely fast, as is confirmed by observation, then the steady state postulate predicts that the first-order dissociation of the dimer will determine the rate of absorption of nitric oxide. Furthermore, the observed first-order rate constant will be independent of nitric oxide pressure. This is shown in Table I for the unsubstituted compound in toluene, and in Table II for the tetranitro compound in acetone. Data in Table II indicate that the dissociation rate constants are independent of glass surface area, light, the accumulation of the product, initial concentration of the dimer, and the presence of unoxidized hydrazine.

TABLE I

FIRST-ORDER DISSOCIATION RATE CONSTANTS AT −28.5 ± 1°[a] FOR 1,1,4,4-TETRAPHENYL-2,3-DIBENZOYLTETRAZANE IN TOLUENE

Pressure of nitric oxide, atm.	$k_1 \times 10^4$, sec.$^{-1}$
0.10	2.0
.23	1.6
.50	1.8
1.00	1.7
1.98	2.0

[a] The poor temperature control arose from the cryostat before it was redesigned, and the temperature variation is responsible for the differences in the rate constants.

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(3) (a) K. Ziegler, P. Orth and K. Weber, *Ann.*, **504**, 131 (1933); (b) C. K. Cain and F. Y. Wiselogle, THIS JOURNAL, **62**, 1163 (1940).

(4) C. F. Baes and W. K. Wilmarth, *J. Chem. Phys.*, **20**, 116 (1952).

(5) H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 3194 (1929), who report a triple point pressure of 165 mm.

(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 48.

(7) W. A. Waters, "Chemistry of Free Radicals," Clarendon Press, London, 1950, p. 148.

TABLE II

FIRST-ORDER DISSOCIATION RATE CONSTANTS FOR THE SUBSTITUTED 1,1,4,4-TETRAPHENYL-2,3-DIBENZOYLTETRAZANES IN ACETONE

R_1	R_2	Pressure of nitric oxide, atm.	Temp., °C.	$k_1 \times 10^4$, sec.$^{-1}$
CH_3	CH_3	0.5	−25.0	56.0
		.5	−30.0	31.3 ± 0.1[a]
		.5	−39.8	8.0
CH_3	H	.5	−20.0	54.7
		.5	−30.0	16.2 ± 0.2
		.5	−40.6	3.36
H	H	.5	−20.0	32.0 ± 0.7
		.5	−30.0	8.3 ± 0.05[b]
		.5	−40.0	2.00
		.5	−40.6	1.64
Br	H	.5	−15.0	45.3
		.5	−20.0	23.9 ± 0.1
		.5	−30.0	6.14
Br	Br	.5	−15.0	34.5
		.5	−20.0	18.2
		.5	−30.0	4.49
		.5	−39.8	0.95
NO_2	H	.5	− 2.0	13.2
		.5	−10.0	4.13
		.5	−20.0	1.05
		.5	−30.0	0.225[c]
		.5	−30.0	.223[c]
NO_2	NO_2	.2	0.0	2.78
		.5	0.0	2.72 ± 0.02
		.7	0.0	2.62
		.5	−10.0	0.629
		.5	−30.0	.022 ± 0.001

[a] The deviations listed are the average deviations of two or more runs. [b] The deviation listed is from eight runs where the variations were: (1) powdered glass was added such that the surface area was doubled; (2) an equal amount of product from a previous run was added before decomposition took place; (3) the cell was taped so that at least 95% of the usual light was excluded; (4) and in the other runs the initial dimer concentration varied from 1.5×10^{-3} to 4.0×10^{-3} *m*, and the unoxidized hydrazine varied from 8×10^{-4} to 4×10^{-3} *m*. [c] These two runs differ in that the initial dimer concentration was held constant, but on the second run enough hydrazine was added to increase its concentration by a factor of four.

Spectrophotometric measurements have shown that the nitro substituted radicals are almost completely complexed by unoxidized hydrazine.[2] However, the red color of the complex disappears as quickly as other uncomplexed radicals when nitric oxide is introduced into the solution. This result indicates that k_2 of equation 2 is still very fast even when it is possible that C, which represents the complex, replaces M. Furthermore the observed first-order rate constant is independent of hydrazine concentration as shown by the identical rate constants at −30° for the dinitro substituted tetrazanes (Table II).

All these facts indicate that equation 2 is the correct formulation and that the observed first-order rate constants are for the dissociation of the dimers to form radicals. Figure 2 shows the temperature coefficient plot of the rate constants, while the energies and entropies of activation[8] are given in Table III (columns 5 and 7).

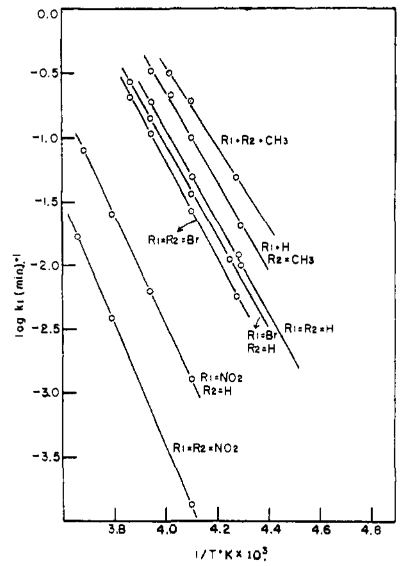

Fig. 2.—Temperature coefficient for first-order dissociation rate constants.

TABLE III

THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION RATE CONSTANTS OF THE SUBSTITUTED 1,1,4,4-TETRAPHENYL-2,3-DIBENZOYLTETRAZANES IN ACETONE AT −30.00°[a]

R_1	R_2	$2(\sigma_1 + \sigma_2)$	$k_1 \times 10^4$, sec.$^{-1}$	$\Delta H_1^{\ddagger}$ kcal./mole. Exptl.	Calcd.	$\Delta S_1^{\ddagger}$, e.u. Exptl.	Calcd.
CH_3	CH_3	−0.680	31.4	15.0	15.2	−10.3	−8.6
CH_3	H	− .340	16.0	15.8	15.6	−8.0	−8.0
H	H	.000	8.29	16.6	16.0	−7.6	−7.5
Br	H	+ .464	6.15	16.6	16.5	−6.6	−6.8
Br	Br	+ .928	4.49	17.2	17.1	−2.7	−5.9
NO_2	H	+2.54	0.214	19.3	19.0	−3.4	−3.2
NO_2	NO_2	+5.08	0.022	21.6	21.9	+1.1	+1.1

[a] The error in the activation energies is ±0.5 kcal. and in the entropy values about ±2 e.u., where these quantities are listed under columns headed (exptl.).

Recombination Rate Constants.—The recombination rate constants, k_{-1} at −30°, and the activation energies and entropies of recombination were calculated from the usual equilibrium expressions in equation 3, using the determined quantities K, k_1, ΔH^0, $\Delta H_1^{\ddagger}$, ΔS^0 and $\Delta S_1^{\ddagger}$, from this and the preceding paper.[2] These quantities are listed in Table IV under the experimental columns (columns 5 and 7).

$$K = k_1/k_{-1} \tag{3a}$$

$$\Delta H^0 = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} \tag{3b}$$

$$\Delta S^0 = \Delta S_1^{\ddagger} - \Delta S_{-1}^{\ddagger} \tag{3c}$$

Applications of the Hammett Equation.—Plots of the Hammett equation for the two constants are shown in Figs. 3 and 4, where the factor 2 is included in the sum of σ-values for the abscissas to account for the symmetry of substitution in the tetrazane molecule. Under each figure are listed the ρ-value; *s*, the standard deviation; *r*, the correlation

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[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

Table IV

Thermodynamic Quantities for the Recombination Rate Constants of the Substituted 1,1-Diphenyl-2-benzoylhydrazyls in Acetone at $-30.00°$

R_1	R_2	$2(\sigma_1 + \sigma_2)$	k_{-1}, l. mole^{-1} sec.$^{-1}$	$\Delta H_{-1}^{\ddagger}$, kcal./moles Exptl.	$\Delta H_{-1}^{\ddagger}$, kcal./moles Calcd.	$\Delta S_{-1}^{\ddagger}$ e.u. Exptl.	$\Delta S_{-1}^{\ddagger}$ e.u. Calcd.
CH_3	CH_3	-0.680	0.59	8.3	8.4	-28.3	-26.6
CH_3	H	$-$ .340	1.7	8.0	7.8	-27.6	-27.6
H	H	.000	2.0	7.4	7.1	-31.3	-28.6
Br	H	$+$ .464	9.8	5.7	6.2	-29.8	-29.9
Br	Br	$+$ .928	26.0	6.0	5.3	-27.8	-31.0

coefficient, and $(\log k^0)_{\text{calcd.}}$ which were all evaluated according to Jaffé.[9]

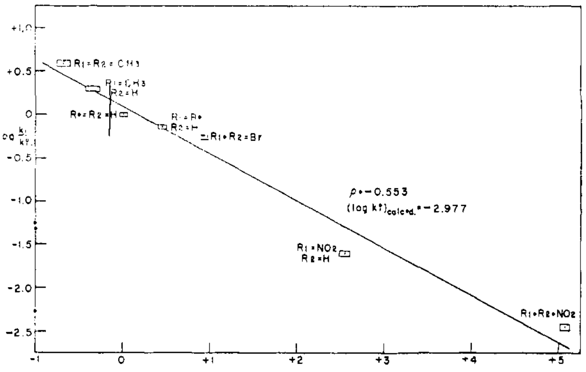

Fig. 3.—ρ–σ plot for dissociation rate constants in acetone at $-30.00°$; $s = 0.17$ and $r = 0.991$.

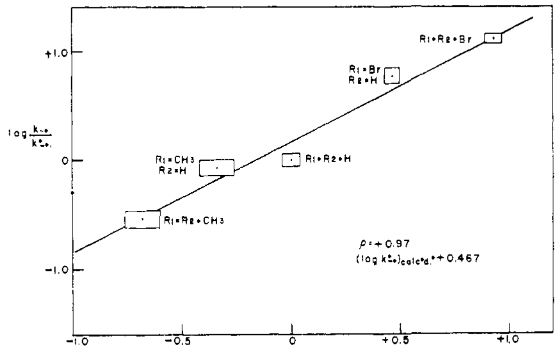

Fig. 4.—ρ-σ plot for recombination rate constants in acetone at $-30.00°$; $s = 0.13$ and $r = 0.986$.

With the use of σ equal to $+0.778$ for the nitro group, a fair fit can be obtained for the dissociation rate constants with a ρ-value of -0.85, s equal to 0.27, and r equal to 0.976. With s equal to 0.17 and r equal to 0.991, a better statistical correlation is shown in Fig. 3 with the high value, σ^* equal to $+1.27$. Furthermore, this latter ρ-value, -0.553, is consistent with the requirements of equation 4,

$$\rho_K = -1.52 = \rho_{k1} - \rho_{k-1} = -0.55 - (+0.97) \quad (4)$$

a consequence of equation 3a and the Hammett equation, where ρ_K and ρ_{k-1} were necessarily evaluated without the nitro substituents. The rather large value of ρ_K results from the ρ-values of the rate constants which add algebraically because of the reversal of sign for the recombination process.

It is impossible at present to evaluate the generality of ρ-values having opposite signs for forward and reverse steps in a particular equilibrium. In Jaffé's compilation[9] only two systems can be analyzed according to equation 4. In the cyanohydrin formation with benzaldehydes *both* forward and reverse rate steps have positive ρ's, with a negative equilibrium ρ resulting from a larger ρ_{k-1} as compared to ρ_{k1}. Because of the opposite effect of substituents on the equilibrium and forward rate, this system represents an anomalous linear free energy relationship.[10] In the formylation of anilines, the ρ's have opposite signs for forward and reverse steps, with the forward step accounting for 85% of the equilibrium ρ-value. It is interesting that the absolute magnitudes of the ρ-values for forward and reverse steps of both the tetrazane system and the formylation of anilines are not the same, as had been supposed for the benzoic acid ionization.[11]

The successful ρ–σ plot for the dissociation rate constants occurs despite non-constant entropy changes, but the entropies are linear with the enthalpy changes. A similar linear dependence is not apparent in the recombination step, but this arises from the compounded error introduced by the necessary evaluation of $\Delta S_{-1}^{\ddagger}$ as the difference between two other entropy quantities. To circumvent this error, smooth values for the experimental quantities were calculated from equations 5a and c. These equations were evaluated from graphical plots against σ (where σ is equal to $2(\sigma_1 + \sigma_2)$). Such smooth values are shown in Table III (columns 6 and 8), and the agreement of calculated and experimental quantities indicates that there is no distortion of the data beyond the experimental error.

$$\Delta H_1^{\ddagger} = 1.2\sigma + 16.0 \quad (5a)$$

$$\Delta H_{-1}^{\ddagger} = -2.0\sigma + 7.1 \quad (5b)$$

$$\Delta S_1^{\ddagger} = 1.7\sigma - 7.5 \quad (5c)$$

$$\Delta S_{-1}^{\ddagger} = -2.6\sigma - 28.7 \quad (5d)$$

If the calculated values for ΔH^0, $\Delta H_1^{\ddagger}$, ΔS^0 and $\Delta S_1^{\ddagger}$ from this and the preceding paper[2] are used to calculate the recombination data (Table IV, columns 6 and 8), a linear dependence is apparent. A quantitative statement of such a dependence is expressed for both steps in equation 6, and the significance of these relationships has been discussed in part I.[2]

$$T\Delta\Delta S_1^{\ddagger} = 0.34\Delta\Delta H_1^{\ddagger} \quad (6a)$$

$$T\Delta\Delta S_{-1}^{\ddagger} = 0.31\Delta\Delta H_{-1}^{\ddagger} \quad (6b)$$

Discussion

The results of both the rate and equilibrium enthalpy studies are most simply illustrated by the potential energy diagram in Fig. 5. The zero of the potential energy scale is to be identified with the potential energy of a hypothetical radical which differs from its dimer only with respect to the energy of the bond which has been broken (*i.e.*, all other bonds in the molecule are assumed to remain unchanged during the dissociation process). Motion along the dotted line from right to left would cor-

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(9) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 209.

(11) H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, This Journal, **74**, 4809 (1952).

respond to dimerization of these idealized radicals, with the depth of the potential well being chosen as 60 kcal./mole, the nitrogen–nitrogen bond energy in gaseous hydrazine.

The solid lines represent motion along the reaction coördinate for the real monomers. The positions of all the dimers have been superimposed in Fig. 5, and the relative positions of the transition states and radicals determined, respectively, from the activation energies and enthalpies of dissociation. The numerical value of the potential energy of each radical, with a positive sign, represents twice the resonance energy of the radical (the resonance energy of the radical is designated R_R); most of this stabilization must be attributed to the formation of a three-electron bond.[2] In the case of the dibromo substituted hydrazyl this gain in resonance energy has been specified in Fig. 5 by the arrow labeled $2R_R$. To the extent that the approximation is valid that the resonance energy associated with the conjugation of the non-bonding pair of electrons on the α-nitrogen atom with the benzene rings has a constant value for a given dimer and radical, then the separation of the radical energy levels represents differences of resonance energy caused by the effect of substituents on the three-electron bond.

The Hammett equation successfully correlates not only the relative values of the equilibrium constants in the tetrazane system but, as Figs. 3 and 4 demonstrate, is equally applicable to the rates of dissociation and recombination. Combination of equations 3b, 5a and b yields equations 7a and b with the linear relationship now expressed in terms of enthalpy quantities which are closely related to the potential energy diagram under discussion and free from the ambiguity of interpretation inherent in the ρ-values.[2]

$$\Delta\Delta H_1 = 0.37\Delta\Delta H^0 \qquad (7a)$$

$$\Delta\Delta H_{-1} = 0.63\Delta\Delta H^0 \qquad (7b)$$

One of the more striking features which appears in the potential energy diagram, besides the great stabilization of the radicals, is the comparable, but smaller, stabilization of the transition states, since the activation energies for dissociation are approximately 45 kcal./mole less than that required for the formation of the hypothetical radicals. The linear enthalpy relations (equations 7a and b) suggest that the stabilization in each case must arise from a similar mechanism. Evidently the stabilizing effect of the three-electron bond which is fully developed and strongly influenced by substituents in the radical has partially developed at the transition state where it is also substituent sensitive. The constants of equations 7a and b might be taken as a measure of the degree of development of this stabilizing force at the transition state. The values of 0.37 and 0.63 for the forward and reverse rates show, as far as sensitivity to substituent is concerned, that the formation of the three-electron bond is less than half complete at this point.

It is evident from Fig. 5 and Table IV that recombination of the hydrazyl radicals requires an activation energy of 5–8 kcal./mole. An activation energy of the same order of magnitude has been observed for the triphenylmethyl radicals[3a] and has been attributed to the steric repulsion between the two large triphenylmethyl units.[12] This explanation would not seem to be applicable to the tetrazane system since molecular models suggest that the dimers are relatively strain free. Moreover, with this explanation, a considerable variation in activation energy would not be expected by varying the substituent at a position far removed from the bonding site.

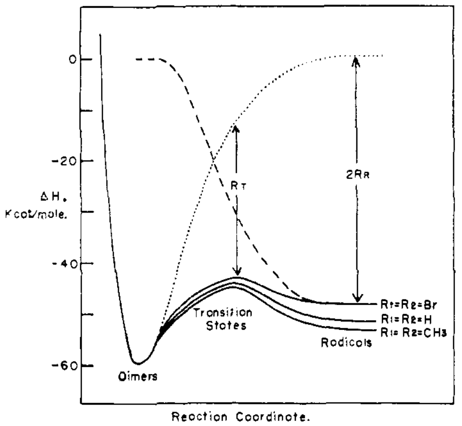

Fig. 5.—Schematic potential energy diagram: . . ., hypothetical dissociation curve; —, actual dissociation curves; - - -, resonance energy curve.

Reference to Fig. 5 suggests an alternate explanation for the activation energy for the hydrazyl recombination, and is based on the difference in resonance energy described above associated with the extent of three-electron bond formation in the transition state as compared to the radicals. As a consequence of this difference in stabilization, energy must be provided to the radicals as they approach the transition state to compensate for their loss in resonance energy. Some energy will be provided by the partial formation of the new nitrogen–nitrogen bond but, if this is insufficient to compensate for the loss of resonance energy, as is evidently the case, the remainder must be furnished in the form of activation energy.

These considerations can be clarified by further reference to Fig. 5. The dotted line, as already mentioned, represents the formation of an idealized radical incapable of stabilization by three-electron bonding. In the case of a single radical, the dibromo substituted hydrazyl, motion along the dashed line from right to left qualitatively represents the loss in three-electron resonance energy as the dimer is produced (similar curves for the other radicals, each starting at the individual radical energy level and all converging to the same point of zero potential energy, have been omitted for the sake of clarity). The difference between the dashed resonance energy curve and the dotted bond energy curve would define the curve for actual recombination of this particular radical. The arrow R_T is included to specify at the transition state the three-electron resonance, a quantity which is non-determinable since the extent of bond formation at this point is unknown.

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(12) M. Szwarc, *Disc. Faraday Soc.*, **2**, 39 (1947); N. Luft, *J. Chem. Phys.*, **21**, 754 (1953).

The premise that differences in resonance energies determine the activation energies to the transition state helps explain the necessary use of the σ^*-value for the nitro group to correlate the dissociation rate constants. The two values of σ for the nitro group usually are associated with the absence or presence of a mesomeric effect involving a pair of electrons in the side chain. For this system, a mesomeric effect that could remove the lone pair of electrons on the α-nitrogen atom would tend to inhibit the stabilization of the transition state, because these electrons are necessary for the three-electron resonance. This argument suggests the use of the σ^*-value for the unknown equilibrium constants of the nitro-substituted compounds.[2]

The role of the lone pair of electrons on the α-nitrogen atom as the reaction proceeds is demonstrated in Fig. 6, where schematic hybridizations are shown for the radicals, dimers and transition states. The structure of the radicals may be inferred from the restrictions imposed by the three-electron bond, and the resonance of the lone pair of electrons on the β-nitrogen atom with the carbonyl group. The picture of the radical in Fig. 6a indicates that the N–N–C atom configuration and its terminal bonds would be similar to allene. The β-nitrogen has an sp-hybridization to provide two π-orbitals, one for the three electron bond (in the plane of the paper) and the other for the carbonyl resonance (at right angles to the plane). The partial double bond character involved in this configuration prevents rotation about both the N–N and C–N bonds.

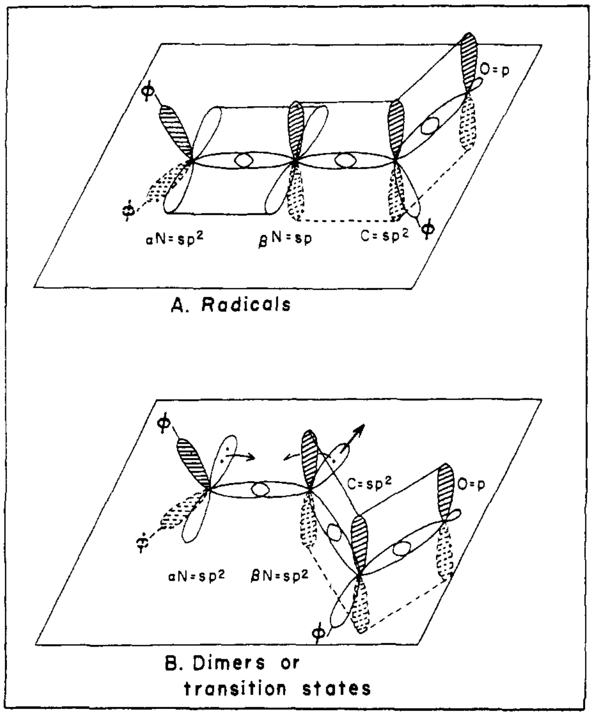

Fig. 6.—Hybridization diagram: Open orbitals are in the plane, full shaded orbitals are above the plane, and half shaded orbitals are below the plane of the paper. The orbitals for the oxygen atom represent only those involved in bonding.

The diagram for the dimer (Fig. 6b) represents only half the molecule, with the straight arrow on the β-nitrogen indicating the orbital involved in the bond to be ruptured. The α-nitrogen of the dimers would be between p^3 and sp^2 hybridization, with only the latter demonstrated in Fig. 6b, depending upon the degree of participation of its lone pair of electrons with the phenyl ring resonance. The two substituted phenyl rings are pictured as out of the plane of the paper, but there is restricted free rotation about the α–β nitrogen bond, damped to some extent by interference of the mirror half of the molecule. In the dimer structure, the carbonyl carbon atom is in the plane of the paper with its p-orbital parallel to the p-orbital (perpendicular to the plane) of the nitrogen atom, thus forming a molecular orbital which includes the nitrogen, carbon and oxygen atoms.

The requirement for the formation of the transition state from the dimer is the more complete transformation of the α-nitrogen atom to an sp^2-hybrid to make its lone pair of electrons available for the start of the three-electron resonance. The transition state is similar to the dimer (Fig. 6b) and differs from it only with respect to non-rotation about the α–β nitrogen bond. The substituted phenyl rings are now necessarily *fixed* out of the paper so that the p-orbital of the α-nitrogen atom is in the same plane as the bond to be broken, allowing for three-electron resonance to begin as the bond breaks. The full and half curved arrow in Fig. 6b indicate, respectively, the shift of a pair and a single electron in the transition state. For the radicals to form the transition state, the carbonyl carbon atom must bend forward to form an angle with respect to the β-nitrogen atom to make the p-orbital on that atom available for bonding to the other radical.

In part I[2] it was demonstrated that the large positive entropy of dissociation for systems of this type is due to the conversion of vibrational degrees of freedom in the dimer to translational and rotational degrees of freedom in the radicals. This effect appears as a large negative activation entropy of recombination, since it is necessary to bring the radicals together to form the transition states. The small activation entropies of dissociation indicate that the transition states are similar to the dimers (Fig. 6b). In gas phase unimolecular decompositions for large molecules, a tendency toward positive entropies is usually observed, reflecting a looseness in the transition state resulting from the many degrees of freedom of a complex species of high energy. The trend toward negative entropies for the tetrazane dissociation, in contradistinction, probably arises from the one or two restricted configurations which actually lead to decomposition in a transition state of low energy.

In contrast to the hexaphenylethane system,[13] the equilibrium constants for dissociation of the tetrazanes are markedly dependent on solvents, with polar solvents increasing the dissociation.[14] This result is consistent with the formation of the

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[13] K. Ziegler and L. Ewald, *Ann.*, **473**, 194 (1929).

[14] S. Goldschmidt and J. Bader, *ibid.*, **473**, 137 (1929); A. Wasserman, *J. Chem. Soc.*, 621 (1942).

charged form of the three-electron bond[2] which might be stabilized by solvation in polar solvents. The rates of dissociation also would increase in the same direction, as demonstrated by the increased rate in acetone as compared to toluene for the unsubstituted compound. It is possible that a process of desolvation partially contributes to the recombination activation energies, but the question of the effect of solvation for any of the steps could be answered only by a complete study in a series of solvents.

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[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

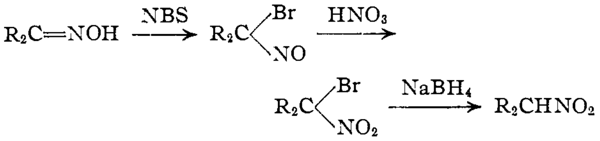
Peroxytrifluoroacetic Acid. VI. The Oxidation of Oximes to Nitroparaffins[1,2]

BY WILLIAM D. EMMONS AND ANGELO S. PAGANO

RECEIVED MARCH 14, 1955

Under suitable conditions peroxytrifluoroacetic acid has been found to be a general reagent for oxidation of oximes to nitroparaffins. The reagent is particularly valuable for preparation of secondary nitroparaffins.

It has been found that under the proper conditions peroxytrifluoroacetic acid is a remarkably efficient and general reagent for oxidation of oximes to nitroparaffins. Previous methods of effecting this reaction have been rather unsatisfactory. Bamberger has, for example, reported the oxidation of benzaldehyde oxime to phenylnitromethane, but the yield was very low and a complex mixture of products was obtained.[3] In a recent series of papers Iffland has described a three-step procedure for conversion of oximes to nitroparaffins.[4] This procedure is based on the bromination of the oxime to the bromonitroso compound with N-bromosuccinimide, oxidation of this to the bromonitroparaffin with nitric acid and finally reduction of the bromonitroparaffin with sodium borohydride. However, this procedure is rather tedious and the yields, particularly in the aliphatic series, are frequently poor. In contrast, the procedures employing peroxytrifluoroacetic acid are one-step reactions which generally may be carried out in fairly good yields.



$$R_2C{=}NOH \xrightarrow{NBS} R_2C\begin{smallmatrix}\diagup Br\\ \diagdown NO\end{smallmatrix} \xrightarrow{HNO_3} R_2C\begin{smallmatrix}\diagup Br\\ \diagdown NO_2\end{smallmatrix} \xrightarrow{NaBH_4} R_2CHNO_2$$

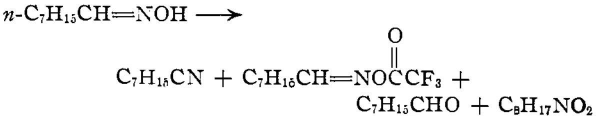
It was found initially in this work that the oxidation of those oximes which yielded resonance stabilized *aci*-nitroparaffins could be carried out using peroxytrifluoroacetic acid in typical procedures which had been developed previously for oxidation of anilines and nitrosamines.[5] Thus the oxidation of diethyl oximinomalonate gave diethyl nitromalonate in 66% yield when carried out in trifluoroacetic acid as solvent. In similar fashion oximinomalonamide was converted to nitromalonamide in 49% yield and phenylglyoxal aldoxime to ω-nitroacetophenone in 76% yield. The oxidation of α-oximinoacetoacetic ester yielded ethyl nitroacetate in 40% yield and also some oxalic acid.[6] In all of the cases described here, the *aci*-nitroparaffin which presumably is formed as the first product of the oxidation is relatively stable and is not destroyed before a prototropic shift to form the nitroparaffin takes place.

$$HON{=}C(COOC_2H_5)_2 \xrightarrow{CF_3CO_3H} NO_2CH(COOC_2H_5)_2$$

$$C_6H_5COCH{=}NOH \xrightarrow{CF_3CO_3H} C_6H_5COCH_2NO_2$$

$$CH_3COC{=}NOH(COOC_2H_5) \xrightarrow{CF_3CO_3H} NO_2CH_2COOC_2H_5$$

The oxidation of monofunctional oximes such as *n*-octyl aldehyde oxime with peroxytrifluoroacetic acid in chlorinated solvents was a completely unsatisfactory reaction. This oxime yielded on treatment with anhydrous peroxytrifluoroacetic acid in ethylene chloride at reflux a complex mixture of products consisting of caprylonitrile, the trifluoroacetate ester of the oxime, *n*-octyl aldehyde and some 1-nitroöctane. All of the components of the mixture were not characterized completely; however, infrared spectra of the crude mixture and its partially fractionated components indicated that substantial amounts of each of the four products mentioned above were present. The nitrile presumably originated from elimination of trifluoroacetic acid from the oxime trifluoroacetate. The aldehyde may have come from hydrolysis of the oxime or, as is more likely the case, from a Nef reaction of the *aci*-nitroparaffin. In order to avoid formation of the oxime trifluoroacetate and the nitrile derived from it, the oxidation of *n*-octyl aldehyde oxime was repeated in ethylene chloride using a disodium hydrogen phosphate buffer to scavenge trifluoroacetic



$$n\text{-}C_7H_{15}CH{=}NOH \longrightarrow C_7H_{15}CN + C_7H_{15}CH{=}NO\overset{O}{\overset{\|}{C}}CF_3 + C_7H_{15}CHO + C_8H_{17}NO_2$$

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

[2] For the preceding paper in this series, see W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

[3] E. Bamberger, *Ber.*, **33**, 1781 (1900).

[4] D. C. Iffland, *et al.*, THIS JOURNAL, **75**, 4044 (1953); D. C. Iffland and G. X. Criner, *ibid.*, **75**, 4047 (1953); D. C. Iffland and Teh-Fu Yen, *ibid.*, **76**, 4083 (1954).

[5] W. D. Emmons, *ibid.*, **76**, 3468, 3470 (1954).

[6] An oxidation of ethyl oximinoacetoacetate to ethyl nitroacetate in 61% yield has been reported previously; V. M. Rodionov, I. V. Machinskaya and V. M. Belikov, *Zhur. Obshchei Khim.* **18**, 917 (1948).