The ether solution was treated with Norit and the product crystallized from ether to give a product with m. p. 200–205°, dec.; yield 4.2 g.

Anal. Calcd. for $C_{27}H_{39}O_3Br$: C, 66.0; H, 8.0. Found: C, 65.8; H, 8.1.

Reduction of Bromo-dehydro-$\Delta^{4,5}$-isosarsasapogenone with Sodium and Ethanol.—To a boiling solution of 4 g. of bromo-dehydro-$\Delta^{4,6}$-isosarsasapogenone in 400 cc. of absolute ethanol was added 20 g. of sodium in small pieces over a period of one hour. Water was added and the precipitated solid taken up in ether, washed well with water and the ether evaporated. The residue was dissolved in a small amount of ethanol and to this was added a solution of 8 g. of digitonin in 400 cc. of 80% ethanol. After standing overnight the digitonide was collected, washed and dried; yield 6.2 g. This was decomposed with pyridine in the usual manner. The product was treated with Norit in methanol and crystallized from ether and methanol to give white crystals, m. p. 202–204°. A mixture with neotigogenin, m. p. 198–200°, melted at 174–185°. A mixture with sarsasapogenin, m. p. 199–201°, melted at 165–174°.

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.6. Found: C, 77.8; H, 10.5.

With boiling acetic anhydride the product gave an **acetate** which crystallized from methanol as white plates, m. p. 202–204°. When mixed with tigogenin acetate, m. p. 203–204° it gave no depression in melting point.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 75.6; H, 9.9.

Isomerization of Neotigogenin into Tigogenin.—A solution of 100 mg. of neotigogenin in 20 cc. of ethanol and 2 cc. of concentrated hydrochloric acid was refluxed for eighty hours. Water was added and the product was crystallized from methanol–acetate, methanol and ethanol to give a product, m. p. 202–204°. When mixed with tigogenin, m. p. 204–206°, it melted at 203–206°. When mixed with neotigogenin of m. p. 199–201°, it melted at 180–186°.

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.6. Found: C, 77.7; H, 10.6.

When refluxed with acetic anhydride it gave an **acetate** which when crystallized from methanol melted at 202–204°. When mixed with tigogenin acetate, m. p. 203–205°, it melted at 203–205°.

Anal. Calcd. for $C_{29}H_{46}O_4$: C, 75.9; H, 10.1. Found: C, 75.8; H, 10.1.

We wish to thank Parke, Davis and Company for their generous help and assistance in the various phases of this work.

Summary

Isosarsasapogenin has been converted to tigogenin, indicating that the tigogenin side chain is of the "iso- configuration."

Neotigogenin upon isomerization with hydrochloric acid is converted into tigogenin.

STATE COLLEGE, PENNA. RECEIVED FEBRUARY 2, 1940

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Divalent Nitrogen. I. The Rate of Dissociation of Tetraphenylhydrazine[1]

BY C. K. CAIN[2] AND F. Y. WISELOGLE

The successive substitution of the hydrogen atoms of ethane by phenyl groups weakens the ethane carbon–carbon linkage to such an extent that hexaphenylethane in solution undergoes rapid dissociation into free radicals at 0°. This marked decrease in the bond strength has been attributed in part to stabilization of the resulting triphenylmethyl radicals through resonance of the odd electrons in the aromatic nuclei, resonance which is not possible in hexaphenylethane.[3]

If stabilization of triarylmethyl radicals through increased resonance is responsible for dissociation in hexaarylethanes,[4] then it seems reasonable to predict that substitution by aryl groups of the hydrogen atoms of any simple dimeric molecule would weaken the central bond of the compound. An accumulation of aryl groups could lead to compounds which would dissociate at moderate temperatures to give relatively stable radicals. Indeed Wieland has attributed many of the reactions of tetraarylhydrazines, $R_2N\text{-}NR_2$, to preliminary dissociation into free radicals, $R_2N\text{-}$, in which the nitrogen atom is divalent.[5] We have now undertaken a study of substituted hydrazines in order to determine the energetics of this dissociation process and thereby to determine the effect on the strength of the N-N bond of substituting various groups for hydrogen atoms. In this paper we report measurements of the rate of dissociation of tetraphenylhydrazine and from these data a calculation of the activation energy for the formation of diphenylnitrogen radicals.

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(1) From a dissertation submitted by C. K. Cain in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University.

(2) E. I. du Pont de Nemours and Co. Fellow, 1938–1939.

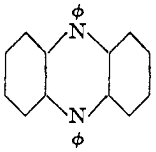
(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 367 (1933).

(4) Recently the importance of resonance as a factor in promoting dissociation of polyarylethanes has been questioned. See, for example, Marvel, Mueller and Ginsberg, THIS JOURNAL, **61**, 2008 (1939). That resonance plays some part in stabilizing the radicals, however, is not disputed.

(5) Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, 1913, pp. 71–78.

Properties and Reactions of Tetraphenylhydrazine.—Tetraphenylhydrazine, prepared from diphenylamine by oxidation, is a colorless crystalline product melting with decomposition at 165–170° to a greenish-brown liquid. Solutions give the same color when heated to approximately 70°; at this temperature tetraphenylhydrazine rapidly undergoes disproportionation (Equation 1).[6]

$2(C_6H_5)_2N—N(C_6H_5)_2 \longrightarrow$



$+ 2(C_6H_5)_2NH$ (1)

Solutions of tetraphenylhydrazine absorb nitric oxide at 100° to give quantitative yields of N-nitrosodiphenylamine, a product which is also obtained by the action of nitrous acid on diphenylamine (Equation 2).[6] The formation of N-nitrosodiphenylamine

$$(C_6H_5)_2N—N(C_6H_5)_2 + 2NO \rightleftharpoons$$

$$2(C_6H_5)_2N—NO \xleftarrow{-2H_2O} 2(C_6H_5)_2NH + 2HONO \quad (2)$$

from nitric oxide is a reversible reaction since at 130° the nitric oxide is evolved in yields up to 95% of the theoretical. Although tetraphenylhydrazine does not react with gaseous oxygen, a reagent for trivalent carbon radicals, further evidence for dissociation was reported in the reaction with triphenylmethyl to give a coupling product of the two radicals (Equation 3)[6]

$$(C_6H_5)_2N—N(C_6H_5)_2 + 2(C_6H_5)_3C— \xrightarrow{100°} 2(C_6H_5)_3C—N(C_6H_5)_2 \quad (3)$$

Rate of Dissociation of Tetraphenylhydrazine.—In order to measure the rate of dissociation of tetraphenylhydrazine it was necessary to find a reagent which would react rapidly and irreversibly with the free diphenylnitrogen radicals but at a negligible rate with the undissociated tetraphenylhydrazine. The rate of the over-all reaction would thus be limited to that of the slowest step and therefore a measure of the rate of the dissociation process. Ziegler, Orth and Weber used nitric oxide successfully to measure the rate of dissociation of hexaphenylethane at temperatures from −20° to +10°[7]; if the partial pressure of nitric oxide was greater than about 0.2 atmosphere the rate of absorption was independent of the pressure and identical with the rate of reaction of hexaphenylethane with iodine or oxygen, proof that the rate-controlling step in each case was the dissociation process. Accordingly, we first selected the reaction of tetraphenylhydrazine with nitric oxide to determine whether the rate-controlling step in this case was the dissociation process.

Experimental

The gas absorptions were carried out in an air thermostat of inside dimensions 16″ × 19″ × 30″ (64 × 79 × 120 cm.) provided with rapid air circulation and containing a bimetallic thermoregulator capable of maintaining temperatures from 50 to 120° constant to within ±0.05°. Temperature control was achieved by using two electrical heating units of which one, carrying 75 to 500 watts, was manually operated to give the approximate temperature and the other, carrying 50 to 200 watts, was operated by the thermoregulator. The temperatures were read on a short stem thermometer graduated to 0.2° and calibrated against a thermometer certified by the Bureau of Standards.

A 200-cc. round-bottomed flask provided with an interchangeable ground glass joint was fastened by a spring clamp to an oscillating shaking mechanism. The thermometer was fastened to the thermostat so that the bulb was a few cm. from the center of the flask. The flask was connected by means of heavy rubber and glass capillary tubing through a T-stopcock to the top of a 100-cc. gas buret (Fig. 1). The buret communicated with a parallel glass leveling tube open at the top and leading through a stopcock into a reservoir of diethyl phthalate which was used as the retaining liquid. The glass leveling tube was connected to the buret by means of a rubber stopper which was protected from the retaining liquid by a layer of mercury. The diethyl phthalate was forced up into the buret and leveling tube by applying air pressure to the reservoir and temporarily opening the stopcock. When the level of liquid was the same in the buret and leveling tube the pressure within the system was equal to that outside. By varying the air pressure on the reservoir and by manipulating the stopcock this condition was maintained throughout each run. This design allowed the use of a light organic liquid sensitive to pressure changes within the system but avoided any direct contact between the organic liquid and rubber. The tedious manipulation of a leveling bulb also was eliminated.

o-Dichlorobenzene was used as the solvent for the reaction. Preliminary experiments indicated that o-dichlorobenzene did not react with nitric oxide at any of the temperatures used in the rate studies. The technical product containing 5% of the para isomer was fractionated and the portion distilling at 180–181° (760 mm.) was retained.

Tetraphenylhydrazine was prepared according to the general directions in Gattermann.[8] Mechanical stirring was used during the addition of the potassium permanganate and the product was recrystallized from benzene and

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[6] Wieland, *Ann.*, **381**, 200 (1911). ϕ represents the phenyl radical.

[7] Ziegler, Orth and Weber, *ibid.*, **504**, 131 (1933).

[8] Gattermann, "Laboratory Methods of Organic Chemistry," The Macmillan Co., New York, N. Y., 1937, p. 355.

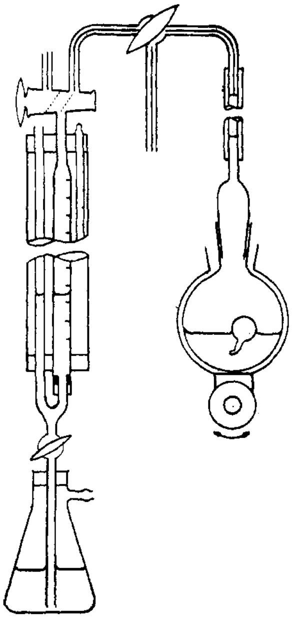

Fig. 1.—Apparatus for measuring rate of absorption of gas at constant pressure.

alcohol. The color on the surface of the crystals was removed by washing the filtered product on the funnel with cold ether. The recorded melting point (144°) is not significant. If the melting point tube was plunged into a preheated bath at this temperature there was a lag of about thirty seconds before the solid suddenly melted. This time lag was reduced at higher temperatures until at 165–170° essentially instantaneous melting took place. The product was dried at 50° under reduced pressure and was used at once for the rate measurements since the solid slowly acquired a green color on standing.

Nitric oxide was prepared by the action of diluted sulfuric acid (1/1) on a solution of sodium nitrite, the nitrogen dioxide being removed by washing the gases with 10% sodium hydroxide solution. The nitric oxide was stored in a gasometer over 1% sodium hydroxide solution, and was dried before use by passage through a tube containing soda-lime. Synthetic mixtures of known volumes of nitric oxide and nitrogen were prepared and stored in gasometers.

In a typical run the flask containing 25 cc. of solvent and a few glass beads was placed in the thermostat at the desired temperature. In order to remove any oxygen dissolved in the solvent the flask was repeatedly evacuated and filled with nitrogen. In the meantime approximately 0.34 g. of tetraphenylhydrazine was introduced into a previously weighed thin-walled glass bulb. The bulb was weighed, then evacuated, filled with nitrogen and sealed. After the flask and solvent had attained the temperature of the thermostat the sample was carefully introduced. Any air which entered the system at this time was removed by evacuation and displacement by nitrogen. The nitrogen was immediately displaced by nitric oxide of known partial pressure and the gas buret was filled with nitric oxide at a pressure of one atmosphere. The T-stopcock was turned to shut off the nitric oxide supply and to open the system to the buret. As soon as the buret reading remained constant for two minutes while the flask was gently shaken, an indication of thermal equilibration, the bulb was broken by increasing the speed and eccentricity of shaking to that maintained throughout the run. The initial buret reading was taken the instant the bulb broke and was usually 0.3 cc. greater than the reading immediately before breaking. The increase in volume undoubtedly arose from the pressure built up within the bulb at the elevated temperature. Absorption of gas began immediately and buret readings were taken at regular, convenient time intervals.

The theoretical absorption was calculated from the equation

$$V = 370.8w(t + 273)/P$$

where w is the weight of the sample, t the temperature of the gas buret and P is the corrected barometric pressure in mm. The coefficient 370.8 is the value of $2 \times 760R/M$, where R is the gas constant, 82.07, M the molecular weight of tetraphenylhydrazine, 336.2, and the factor 2 arises from the absorption of two moles of nitric oxide by one mole of tetraphenylhydrazine.

In Table I, columns 1, 2 and 3, are recorded typical data obtained in a representative experiment.

Results and Discussion

Nature of the Reaction.—In Fig. 2 are plotted the time rates of absorption of nitric oxide at 95.15° by 0.04 molar solutions of tetraphenylhydrazine in *o*-dichlorobenzene at various nitric oxide pressures. From an inspection of the curves it is evident that the absorption of nitric oxide did not approach two moles, required for the formation of N-nitrosodiphenylamine, but stopped at 75–95% of this value. We were first inclined to attribute this apparent incomplete

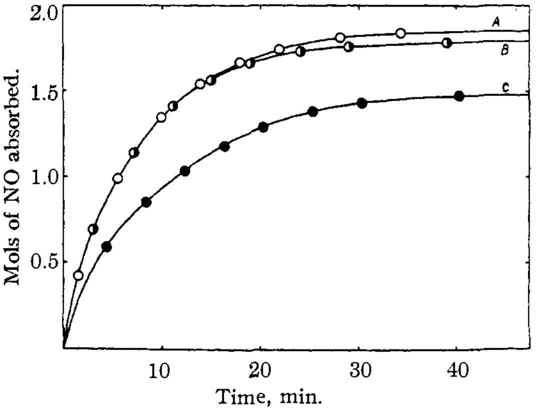

Fig. 2.—Rate of absorption of nitric oxide by solutions of tetraphenylhydrazine in *o*-dichlorobenzene at 95.15°: Curve A, pNO = 1.0 atm.; curve B, pNO = 0.2 atm.; curve C, pNO = 0.1 atm.

absorption to redissociation of the N-nitrosodiphenylamine and attainment of equilibrium (Equation 2). Although Wieland has established the dissociation of N-nitrosodiphenylamine into nitric oxide at 130°, a sample of the reaction product dissolved in *o*-dichlorobenzene at 100° proved perfectly stable and no nitric oxide was evolved.

TABLE I

ABSORPTION OF NITRIC OXIDE BY TETRAPHENYLHYDRAZINE: TYPICAL DATA OBTAINED IN REPRESENTATIVE EXPERIMENT

Tetraphenylhydrazine, 0.3949 g.; 25 cc. of *o*-dichlorobenzene; barometer, cor., 760.7 mm.; buret temp., 23.0°; pNO, 0.20 atm.; temp. of thermostat, 95.15°; theoretical absorption, 57.0 cc.; rate constant, from slope of curve in Fig. 3, 0.1285 min.$^{-1}$.

Time, min.	Buret reading, cc.	Absorption, cc.	Volume yet to be absorbed, cc.	$-\text{Log } (1 - Z)$	$= kt/2.3$
0.00	85.2	0.0	51.5	0.000	0.000
.73	80.6	4.6	46.9	.041	.041
1.73	74.9	10.3	41.2	.097	.097
2.73	69.9	15.3	36.2	.153	.153
3.73	65.5	19.7	31.8	.209	.208
4.73	61.6	23.6	27.9	.266	.264
5.73	58.2	27.0	24.5	.323	.320
6.73	55.2	30.0	21.5	.379	.376
7.73	52.7	32.5	19.0	.433	.432
8.73	50.4	34.8	16.7	.489	.488
9.73	48.4	36.8	14.7	.543	.543
11.73	45.1	40.1	11.4	.655	.655
13.73	42.6	42.6	8.9	.762	.767
15.73	40.6	44.6	6.9	.873	.879
17.73	39.1	46.1	5.4	.979	.991
19.73	37.8	47.4	4.1	1.100	1.103
24.73	35.9	49.3	2.2	1.369	1.414
29.73	35.1	50.1	1.4	1.566	1.661
39.73	34.3	50.9	0.6	1.934	2.220
∞	33.7	51.5	0.0		

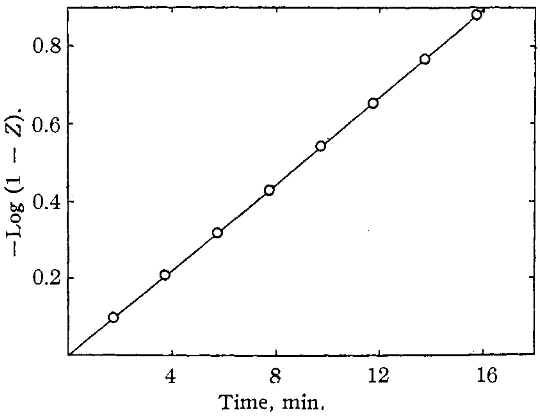

Fig. 3.—Rate of nitric oxide absorption by tetraphenylhydrazine. A plot of data in Table I.

Moreover, the fraction of the theoretical absorption of nitric oxide decreased as the time increased between the introduction of the sealed sample into the reaction flask and the beginning of the reaction. In an extreme case a bulb containing solid tetraphenylhydrazine in a nitrogen atmosphere was maintained at 100° for one hour; at the end of this period the sample was colored dark green and had partially liquefied, indicating extensive decomposition. When the bulb was broken in the absorption flask and the sample dissolved, the total absorption of nitric oxide was only 5.7% of the theoretical. It is evident, therefore, that tetraphenylhydrazine in the solid state undergoes extensive thermal decomposition at 100° to give products which do not react with nitric oxide.

That the reaction between nitric oxide and tetraphenylhydrazine was quantitative was shown in another experiment by dissolving a weighed sample of tetraphenylhydrazine in *o*-dichlorobenzene at 18°, a temperature at which no reaction took place; the solution, in the presence of nitric oxide, was warmed to 100° and maintained at this temperature for one hour. When the reaction mixture was again cooled to 18° the decrease in volume indicated an absorption of 99% of the theoretical amount of nitric oxide. A 94% yield of N-nitrosodiphenylamine was isolated from the reaction mixture on removal of the solvent; the product was identified through a determination of the melting point of a mixture with an authentic sample prepared from diphenylamine.

The reaction between tetraphenylhydrazine and nitric oxide, therefore, is stoichiometric and irreversible at temperatures up to 100°; moreover, the rate of absorption of nitric oxide, at 1 atm. pressure, is greater than the rate of thermal decomposition in *o*-dichlorobenzene. Because solid tetraphenylhydrazine also undergoes a fairly rapid pyrolysis, however, the true concentration of material present at the start of the reaction, *i. e.*, when the bulb was broken, was considerably less than that calculated from the weight of the sample. This initial concentration of tetraphenylhydrazine was calculated from the total absorption of nitric oxide at the completion of the reaction, using the equation given in the experimental section for calculating the theoretical absorption.

It was, of course, impossible to prevent the undesired pyrolysis of the solid tetraphenylhydrazine in our rate experiments but we reduced to a minimum the time between the introduction of the sample and the breaking of the bulb. This period was rarely more than twenty minutes and under these conditions the absorption approached 85–95% of the theoretical at the higher temperatures and 100% of the theoretical at the lower temperatures.

Mechanism of the Reaction.—If the rate-controlling step involves a direct reaction between tetraphenylhydrazine and nitric oxide, regardless of the mechanism, then the rate must be a function of the nitric oxide concentration. Conversely, if the rate of absorption proves to be independent of the nitric oxide concentration, the nitric oxide cannot be involved in the rate-controlling step. Under the conditions of our experiments the partial pressure of nitric oxide was maintained constant throughout a run; the concentration of dissolved nitric oxide, proportional to the partial pressure, also remained constant since the gas–solution equilibrium was maintained by vigorous shaking. In order to determine the effect of changing the concentration of nitric oxide, therefore, several runs were made at different nitric oxide pressures.

From an inspection of the curves A and B of Fig. 2 it is apparent that the initial rate of absorption is independent of the nitric oxide pressure if this is greater than 0.2 atm. At these relatively high pressures, therefore, the rate-controlling step is a first-order reaction and a direct reaction between tetraphenylhydrazine and nitric oxide is precluded. For very low pressures, however, both the rate and extent of absorption of nitric oxide decrease (Curve C, Fig. 2).

These data, then, parallel those obtained by Ziegler, Orth and Weber for the reaction between hexaphenylethane and nitric oxide at 0°[7]; we believe the mechanisms in the two cases are analogous. The first step in the formation of N-nitrosodiphenylamine is a slow, unimolecular dissociation of tetraphenylhydrazine into free radicals (Equation 4).

$$(C_6H_5)_2N\text{—}N(C_6H_5)_2 \xrightarrow{\text{slow}} 2(C_6H_5)_2N\text{—} \qquad (4)$$

In the absence of any reagent these radicals may undergo recombination to form tetraphenylhydrazine (Equation 5) or they may undergo an irreversible thermal decomposition (Equation 6). In

$$2(C_6H_5)_2N\text{—} \longrightarrow (C_6H_5)_2N\text{—}N(C_6H_5)_2 \qquad (5)$$

$$x(C_6H_5)_2N\text{—} \xrightarrow{\text{fast}} \text{disproportionation products} \qquad (6)$$

the presence of nitric oxide at pressures above 0.2 atm., however, the radicals react exclusively with nitric oxide as fast as they are formed (Equation 7). The rate of absorption of nitric

$$(C_6H_5)_2N\text{—} + NO \xrightarrow{\text{very fast}} (C_6H_5)_2N\text{—}NO \qquad (7)$$

oxide, therefore, depends only upon the rate of formation of the diphenylnitrogen radicals and the over-all reaction is of the first order with respect to tetraphenylhydrazine.

At low partial pressures the small concentration of dissolved nitric oxide results in a decrease in the rate of formation of N-nitrosodiphenylamine (Equation 7); diphenylnitrogen radicals accumulate in the solution and may undergo reactions (5) and (6) as well as (7); the over-all rate becomes a function of the nitric oxide pressure and is less than the rate of dissociation.

For a first-order reaction the time rate of change of concentration may be expressed in the form: $-\log (1 - Z) = kt/2.3$, where Z is the fraction of tetraphenylhydrazine or nitric oxide reacted in time, t, and k is the specific reaction rate constant. In our work the fraction, Z, was determined by dividing the decrease in volume at time t by the total decrease in volume at the completion of the reaction. For such a reaction a plot of $-\log (1 - Z)$ against t should give a straight line the slope of which multiplied by 2.3 is the rate constant. Figure 3 shows such a plot from the data of Table I, and represents a typical evaluation of the rate constant. The precision of the data may be evaluated by comparing columns 5 and 6 of Table I.

Table II shows the effect of changing conditions on the rate constant at 95.15°. It will be noted that the rate constant is independent of the concentration of tetraphenylhydrazine, and of the partial pressure of nitric oxide except at very low values.

TABLE II

VELOCITY OF NITRIC OXIDE ABSORPTION BY TETRAPHENYLHYDRAZINE AT 95.15°

Concn. of tetraphenylhydrazine in moles per liter	Nitric oxide pressure, atm.	Per cent. of theoretical absorption	Rate constant k
0.046	1	82	0.131
.033	1	76	.132
.025	1	89	.127
.042	0.2	90	.128
.019	.2	88	.114
.028	.1	74	.088
Average of all reliable runs made			.130

We have repeated the absorption rate studies at five-degree intervals from 75 to 100° and have verified this unimolecular character of the rate-controlling step at all temperatures; the results are collected in Table III. At the lower temperatures it was inconvenient to allow the reaction to proceed to completion and a more practicable method was adopted for calculating the rate constant. The reaction was carried to approximately 75% of completion and the total absorption of nitric oxide at infinite time was used as a parameter in plotting $-\log (1 - Z)$ against t; that value was chosen which gave no appreciable departure from a straight line and the rate constant was calculated from the slope of this line. This method is illustrated in Fig. 4 where three curves are plotted selecting values for the total absorption 2.5% too high and too low from the value which gave the best straight line. In a few experiments the two methods were compared; the agreement of the rate constants was usually within 2%.

Table III

Velocity of Nitric Oxide Absorption by Tetraphenylhydrazine

Temp., °C.	Av. vel. constant k, min.$^{-1}$	Half-life, min.	No. of runs	Mean error of mean, %
75.20	0.0119	58.3	2	1.7
80.20	.0230	30.2	4	1.7
85.20	.0397	17.5	4	2.5
90.2	.0670	10.4	4	1.8
95.15	.130	5.35	4	1.0
100.10	.222	3.13	5	2.0

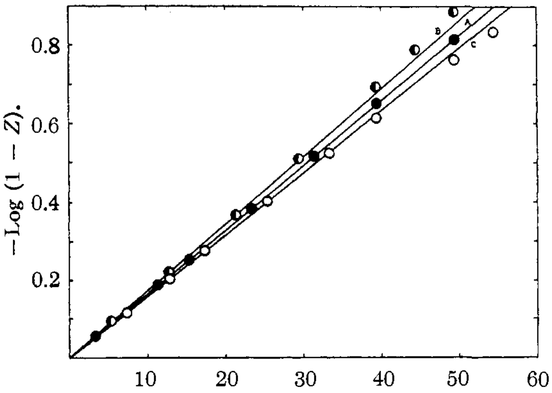

Fig. 4.—Rate of absorption of a 0.04 molar solution of tetraphenylhydrazine in *o*-dichlorobenzene at 85.20° showing alternative method of calculating rate constant: pNO = 1.0 atm.; Curve A, filled circles, total absorption assumed to be 40.0 cc.; Curve B, half-filled circles, total absorption assumed to be 39.0 cc.; Curve C, open circles, total absorption assumed to be 41.0 cc. It is apparent that the curves on either side of A diverge; rate "constants" for the three curves are: for C, 0.0365; for A, 0.0382; for B, 0.0401. The curves are exaggerated to illustrate the principle of the method; in practice absorptions of 39.5 cc. and 40.5 cc. would be assumed. The rate constant was determined from the slope of curve A, which shows no perceptible deviation from a straight line.

The energy of activation, E, for the rate-controlling step was calculated from the Arrhenius equation, $\log k = E/2.3RT + C$, where R is the gas constant, T the absolute temperature and C the integration constant. A plot of log k against the reciprocal of the absolute temperature gave a straight line (Fig. 5) the slope of which multiplied by 2.3 R gave 30 kcal. as the heat of activation. We consider that this value is accurate to ±1.5 kcal.

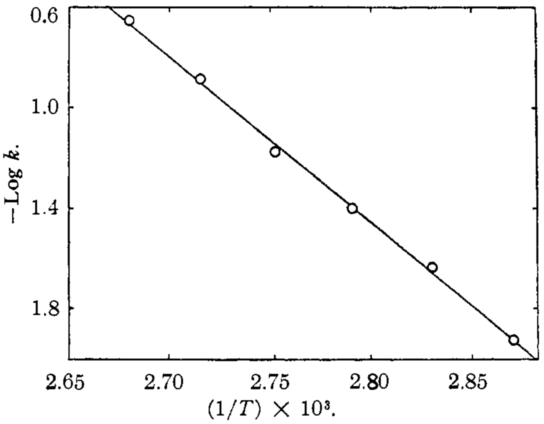

Fig. 5.—The rate of dissociation of tetraphenylhydrazine at different temperatures.

The energy of activation for a dissociation process, E_d, is of considerable significance since it represents a maximum value for the strength of the bond broken and is related to the bond strength, ΔH, by the equation $\Delta H = E_d - E_a$, where E_a is the activation energy for the association of the resulting radicals. The carbon–carbon bond strength in hexaphenylethane, 11.5 kcal.,[9] represents a marked decrease from the normal carbon–carbon bond strength of ethane, 58.6 kcal.,[10] an average reduction of 8 kcal. per phenyl group. The activation energy for the dissociation process likewise decreases as phenyl groups are substituted for hydrogen atoms. The activation energies for the dissociation of pentaphenylethane and hexaphenylethane are, respectively, 27.6 kcal.[11] and 19.5 kcal.[6] It will be noted that the difference, 8 kcal., is identical with

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(9) Ziegler and Ewald, *Ann.*, **473**, 163 (1929).

(10) Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(11) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 359 (1936).

the average effect on the bond strength of replacing a hydrogen atom by a phenyl group.

Recently Hughes, Corruccini and Gilbert[12] have redetermined the heat of combustion of hydrazine, H_2N-NH_2, making possible a calculation of the strength of the normal N–N bond from thermochemical data. From the energy of formation of gaseous hydrazine from the elements, 22.25 kcal., the energy of dissociation of hydrogen, 103.8 kcal.,[13] and the energy of dissociation of nitrogen, 170.2 kcal., the energy of formation of gaseous hydrazine from the atoms may be calculated. This energy, 355.6 kcal., may be considered to be composed of two terms, one involving four N–H bonds and the other involving the N–N bond. If we assume that the average N–H bond strength in hydrazine is the same as in ammonia, 83.9 kcal., the energy of dissociation of hydrazine into divalent nitrogen radicals is 20 kcal. (Equation 8).[14]

$$N_2H_4(g) \longrightarrow 2NH_2^-(g) \qquad \Delta H = 20 \text{ kcal.} \qquad (8)$$

The energy of activation for the dissociation of tetraphenylhydrazine is greater than the energy of dissociation of hydrazine, in marked contrast to the lowering of bond strength and activation energy by substituting phenyl groups for hydrogen atoms in the ethane series. If the substitution of an aryl group for a hydrogen atom in hydrazine lowers the bond strength, then the energy of activation for the coupling of two divalent nitrogen radicals must be inordinately high. A rigorous test of this must await a determination of the energy of dissociation of tetraphenylhydrazine.

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Summary

A study has been made of the kinetics of the reaction between tetraphenylhydrazine and nitric oxide at 75 to 100°. Although solid tetraphenylhydrazine undergoes rapid decomposition at 100°, solutions in *o*-dichlorobenzene absorb nitric oxide quantitatively and irreversibly to give N-nitrosodiphenylamine. For nitric oxide pressures above 0.2 atm. the rate-controlling step is independent of the nitric oxide pressure and is undoubtedly the dissociation of tetraphenylhydrazine into free diphenylnitrogen radicals. The half-life of tetraphenylhydrazine at 100° is 3.1 minutes and the energy of activation for the dissociation is 30 ± 1.5 kcal. This activation energy is 10 kcal. greater than the energy of dissociation of hydrazine calculated from recent thermochemical measurements.

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[12] Hughes, Corruccini and Gilbert, THIS JOURNAL, **61**, 2639 (1939).

[13] The data for the bond strengths in ammonia and for the heats of dissociation of hydrogen and nitrogen were taken from Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1939, and Bichowsky and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[14] This N–N bond strength is 4 kcal. less than that calculated by Pauling who used the average value for the heat of combustion of hydrazine cited in Bichowsky and Rossini (*loc. cit.*). It should be noted that the assumption of the equality of the N–H bond strengths in ammonia and in hydrazine has not received the empirical support which is available for other bonds such as C–H and O–H. We do know that the successive removal of hydrogen atoms from ammonia requires widely different energies. Thus the heat of dissociation of NH, 102.2 kcal., which is accurately known from spectroscopic data is much greater than the average strength of the N–H bonds in ammonia.