

fluoride, but no definite conclusions can be reached concerning variation in the ammonium bands near 3.2μ because of hydrolysis effects. Evidence for

changes in the associational structure of the solvent is found in the 4.7μ region.

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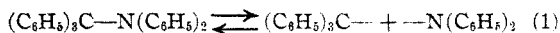
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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE JOHNS HOPKINS UNIVERSITY]

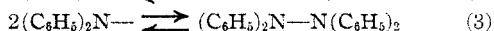
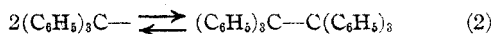
Divalent Nitrogen. II. The Action of Nitric Oxide on Pentaphenylethane¹

BY HENRY SONNEBORN, III, AND F. Y. WISELOGLE

There is abundant qualitative evidence that the compound triphenylmethyldiphenylamine undergoes reversible dissociation in solution at 100° giving triphenylmethyl and diphenylnitrogen radicals (Eq. 1).² Since each of these radicals can dimerize reversibly forming symmetrical com-



pounds (Eqs. 2, 3), the triphenylmethyldiphenylamine at 100° is also in equilibrium with hexa-



phenylethane and tetraphenylhydrazine. In analogous systems the unsymmetrical product generally predominates and it is of considerable interest to evaluate the factors responsible for the stabilization of such unsymmetrical molecules with respect to their symmetrical counterparts.³ A determination of the equilibrium constant for each reaction would make possible a direct calculation of the heat of dissociation which may be taken as the strength of the bond ruptured.⁴ While the heat of dissociation of hexaphenylethane is known,⁵ considerable experimental difficulties

would arise in measuring the equilibrium constants for the other reactions due, for the most part, to the thermal instability of the diphenylnitrogen radical.⁶

A quantity closely related to and generally paralleling the bond strength is the activation energy for the dissociation; this energy is calculated from the rate of dissociation measured at different temperatures. Activation energies for the dissociation of hexaphenylethane⁷ and tetraphenylhydrazine⁸ already have been determined and some time ago we set out to determine the activation energy for the dissociation of triphenylmethyldiphenylamine. We hoped to measure the rate of dissociation by capturing the triphenylmethyl radicals with oxygen in the presence of pyrogallol and measuring the uptake of oxygen. Although this reagent has proved ideally satisfactory for studying rates of dissociation of polyarylethanes,⁸ oxygen and pyrogallol were inapplicable in this case. The quantity of oxygen consumed corresponded, approximately, to one mole per mole of triphenylmethyldiphenylamine in agreement with our expectations. The rate of absorption greatly exceeded that predicted, however, and did not follow the first order law, a requisite behavior if the dissociation reaction had been the rate controlling step.^{2b}

Since oxygen appeared to be excluded as a reagent for studying the rate of dissociation of triphenylmethyldiphenylamine,⁹ we have turned to other possible radical capturing substances. Nitric oxide has been shown to react rapidly and

(1) From a dissertation submitted by Henry Sonneborn, III, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Johns Hopkins University. A portion of this paper was presented before the Division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, April 7-11, 1941. We are indebted to the Hynson, Westcott and Dunning Research Fund for a grant-in-aid covering a part of the cost of this research. Paper I, see ref. 6.

(2) (a) Wieland, *Ann.*, **381**, 200 (1911); (b) Cain, Dissertation, "The Free Diphenylnitrogen Radical," The Johns Hopkins University, 1939.

(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 374 (1933).

(4) It is important to distinguish between the bond strength as defined here and the bond energy as defined by Pauling. The latter "represents not the amount of energy required to break one bond in a molecule, but instead the average amount required to break all the bonds" of a similar type when the molecule is disrupted into atoms. Only for a diatomic molecule are the bond strength and the Pauling bond energy identical. There is considerable experimental evidence, however, that for carbon-carbon single bonds the two quantities are approximately the same except where radicals are stabilized due to resonance. L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, pp. 53, 58.

(5) Ziegler and Ewald, *Ann.*, **473**, 163 (1929); Preckel and Selwood, *This Journal*, **63**, 3397 (1941).

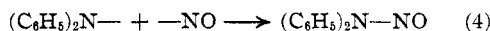
(6) Cain and Wiselogle, *ibid.*, **62**, 1163 (1940) (paper I of this series).

(7) Ziegler, Orth and Weber, *Ann.*, **504**, 131 (1933).

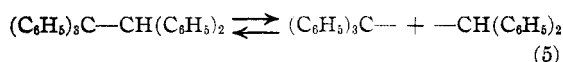
(8) (a) Ziegler, Ewald and Seib, *ibid.*, **504**, 182 (1933); (b) Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936); (c) Bachmann and Osborn, *ibid.*, **5**, 29 (1940); (d) Witten and Wiselogle, *ibid.*, **6**, 584 (1941).

(9) We have subsequently learned that pyrogallol rapidly attacks the undissociated triphenylmethyldiphenylamine liberating a triphenylmethyl radical. By substituting basic oxidation inhibitors, e. g., *p*-phenylenediamine, for pyrogallol first order rate constants were obtained.

irreversibly with diphenylnitrogen radicals at 100° giving the stable diphenylnitrosoamine (Eq. 4)⁶; accordingly we have explored the action of nitric oxide on trivalent carbon radicals



under these conditions. As a convenient source of such radicals, we have chosen pentaphenylethane, a compound isoelectronic with triphenylmethyl diphenylamine, whose rate of dissociation into triphenylmethyl and diphenylmethyl radicals already has been determined (Eq. 5).^{8b,c}



Nature of the Reaction.—For our studies of stoichiometry and rate, the reaction was carried out at constant temperature and at atmospheric pressure. The solvent and a sealed glass bulb containing a weighed quantity of pentaphenylethane were placed in a reaction flask which in turn was placed in a thermostat. The air within the flask was successively displaced by nitrogen and by nitric oxide and the flask was then connected to a gas buret which was also filled with nitric oxide. When the system had attained constant temperature the flask was shaken mechanically. This shaking served to break the bulb, to dissolve the pentaphenylethane and to ensure saturation of the solution with nitric oxide. The rate and extent of the reaction were followed by measuring the diminution of gas volume within the buret.

At 95° a solution of pentaphenylethane rapidly absorbed nitric oxide, the reaction being essentially complete in thirty minutes. Throughout this time the solution remained transparent and colorless or at most a very light yellow; the gas above the solution also remained colorless thereby indicating the absence of any appreciable amount of reddish-brown nitrogen dioxide. The absorption of gas corresponded accurately to three moles per mole of pentaphenylethane. This behavior, which suggests a single, irreversible sequence of reactions, stands in marked contrast to the action of oxygen or of iodine on pentaphenylethane.^{8b,c} The latter reactions are not stoichiometric in the absence of additives because of complicating side reactions or redissociation of the products formed.

Rate of the Reaction.—In order to determine the order of the over-all reaction we varied the concentration of dissolved nitric oxide by diluting the gas with known percentages of nitrogen.

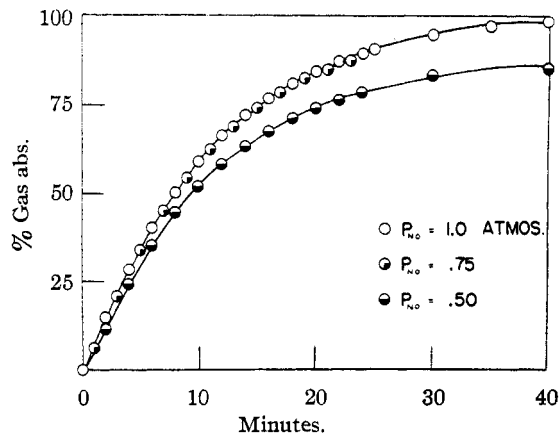


Fig. 1.—Rate of absorption of nitric oxide by 0.024 molar solutions of pentaphenylethane in *o*-dichlorobenzene at 95.45° and at different partial pressures of nitric oxide. The percentage of gas absorption was calculated assuming the stoichiometric ratio of three moles per mole of pentaphenylethane.

In Fig. 1 are plotted the time rates of absorption of gas by pentaphenylethane at 95.45° and at three different nitric oxide partial pressures. From an inspection of the curves it is apparent that a change in the partial pressure of nitric oxide from 1.0 atmosphere to 0.75 atmosphere did not change either the rate or the extent of absorption. At a partial pressure of 0.5 atmosphere the absorption decreased by about seven per cent, however, and there was an appreciable lowering in the rate.

Now any direct reaction between nitric oxide and pentaphenylethane would be expected to follow a second order or perhaps a third order rate law. In such cases the rate of the reaction is proportional to the nitric oxide pressure or to the square of the pressure. When the partial pressure of nitric oxide is one atmosphere, however, the observed rate of reaction is independent of the pressure and any direct attack on the pentaphenylethane by nitric oxide is excluded from consideration.

For a first order reaction the time rate of change of reactant may be expressed in the form, $-\log(1 - Z) = kt/2.3$, where Z is the fraction of pentaphenylethane, or nitric oxide, reacted in time t , and k is the reaction rate constant. 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 2 shows such a plot from a run made at 95.45° under a nitric oxide pressure of one atmosphere. It is evident that a straight line is obtained; the slope is con-

stant throughout at least 80% of the reaction and the rate-controlling step must be first order with respect to pentaphenylethane.

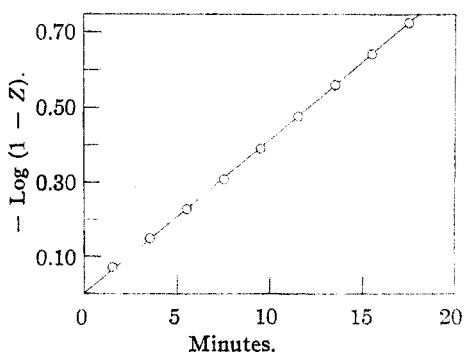


Fig. 2.—Rate of absorption of nitric oxide by 0.024 molar solution of pentaphenylethane in *o*-dichlorobenzene at 95.45° and at one atmosphere pressure of nitric oxide. The rate constant calculated from the slope is 0.0970 min.⁻¹.

We have repeated these runs under different conditions of temperature, pressure and pentaphenylethane concentration and have calculated the rate constants from the slopes of the lines obtained by plotting $-\log (1 - Z)$ against t . These data are collected in Table I. With but one or two unexplained exceptions in every rate de-

termination straight lines were obtained at all temperatures when the nitric oxide pressure was one atmosphere; the extent of absorption averaged within 98% of the stoichiometric ratio of three moles per mole of pentaphenylethane.

It is clear that the rate of absorption of nitric oxide is proportional to the amount of pentaphenylethane present and independent of the nitric oxide pressure when this is one atmosphere. It is reasonable to conclude that the rate controlling step is the slow dissociation of pentaphenylethane into free radicals, a unimolecular reaction (Eq. 5).

From the average values of the rate constants at the four temperatures studied we have calculated the activation energy, E , for the dissociation process using the Arrhenius equation, $-\log k = E/2.3RT + C$, where R is the gas constant, T the absolute temperature and C is a constant of integration. A plot of $-\log k$ against $1/T$ should give a straight line, the slope of which multiplied by $2.3R$ is the activation energy. Figure 3 shows the straight line so obtained from which we have calculated the dissociation activation energy for pentaphenylethane to be 28.2 ± 0.7 kcal.

TABLE I
ACTION OF NITRIC OXIDE ON PENTAPHENYLETHANE

Temp., °C.	Pentaphenylethane concn., molar	Nitric oxide pressure, atm.	Percentage of theoretical absorption	Rate constant, min. ⁻¹	Half-life, min.
90.20	0.024	1.00	100		11.65
90.20	.024	1.00	100		12.05
90.20	.024	1.00	100		12.51
90.20	.024	1.00	100		12.00
90.20	.024	0.50	99		12.60
				Average 0.0570	12.16
95.45	.024	1.00	99		6.83
95.45	.024	1.00	100		7.15
95.45	.024	1.00	99		6.87
95.45	.024	1.00	97		7.15
95.45	.024	1.00	98		7.28
95.45	.024	0.75	100		7.03
95.45	.024	0.75	98		7.31
95.45	.049	1.00	99		6.95
95.45	.049	0.50	93		(9.) ^a
95.45	.034	1.00	99		7.04
				Average 0.0980	7.07
100.40	.024	1.00	101		4.28 ^a
100.40	.024	1.00	97		4.25
100.40	.024	1.00	98		3.98
				Average 0.166	4.17
105.65	.024	1.00	98		2.48
105.65	.024	1.00	97		2.52
105.65	.024	0.50	90		(9.) ^a
				Average 0.277	2.50

Datum not used in computing average rate constant or half-life.

It is of interest to compare the kinetics of the reactions between pentaphenylethane and nitric oxide, oxygen^{8b} and iodine.^{8c} Since each reaction rate has been shown to be first order with respect to pentaphenylethane and independent of the reagent concentration it was to be expected that the kinetics and energetics would prove identical. In Table II are compared the specific rate constants and half-lives calculated for 95.00° as well as the activation energies for the three reactions.

From an inspection of Table II it is clear that the activation energies and reaction rates are in good agreement; nevertheless the differences in

TABLE II

RATE AND ACTIVATION ENERGY FOR DISSOCIATION OF PENTAPHENYLETHANE

Reagent	Rate constant at 95.00°, min. ⁻¹	Half-life at 95.00°, min.	Activation energy, kcal.
Nitric oxide	0.0943	7.35	28.2 ± 0.7
Oxygen and pyrogallol	.0809	8.58	27.6 ± 0.5
Iodine, pyridine and ethanol	.0613	11.3	27.1

reaction rates, small as they are, lie beyond the limit of experimental error. This is not surprising for, although in each reaction *o*-dichlorobenzene was used as solvent, the reaction medium was different in all three cases. For the oxygen reaction it was necessary to add pyrogallol and for the iodine reaction it was necessary to add both pyridine and ethanol. It is likely that pentaphenylethane reacted with these additives to form loose molecular compounds whose dissociation probabilities were less than that of pentaphenylethane alone. In an attempt to test this hypothesis we added pyrogallol to a reaction run using nitric oxide. Unfortunately, however, the character of the reaction was profoundly changed, the total gas absorption decreasing to 1.3 moles per mole of the ethane. We were unable, moreover, to obtain a good first-order rate constant.

Reaction Products.—The absorption of three moles of gas per mole of pentaphenylethane was, despite the stoichiometry, an interesting anomaly. Nitric oxide is a free radical and the dissociation of pentaphenylethane gives two free radicals. Any combination of five free radicals must leave at least one radical in the mixture. To remove this radical by dimerization would necessitate an unattractive mechanism involving at least two

moles of pentaphenylethane and six moles of nitric oxide.

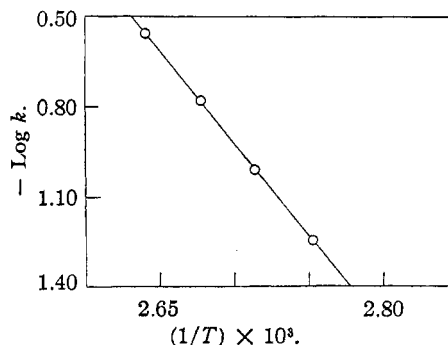


Fig. 3.—The rate of dissociation of pentaphenylethane at different temperatures.

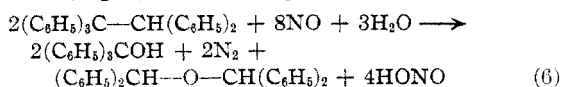
It seemed likely, therefore, that an even number of moles of nitric oxide had been absorbed but that some gas had been evolved simultaneously so that the apparent absorption of three moles represented the difference. That no water vapor was liberated during the reaction was demonstrated by dissolving a weighed quantity of pentaphenylethane in *o*-dichlorobenzene at 0°, a temperature at which no dissociation took place; the solution was warmed to 100° in the presence of nitric oxide until absorption was essentially complete and then cooled to the original temperature. The net absorption measured at 0° was three moles per mole of pentaphenylethane excluding the liberation of any condensable gas at the higher temperature.

In order to demonstrate the liberation of permanent gas during the reaction, the gas mixture remaining at the conclusion of a rate run was passed through potassium permanganate solution which absorbed all of the nitric oxide. The residual gas was equal to one-third of the net absorption, corresponding to one mole per mole of pentaphenylethane. The gas would not support combustion, a property of nitrous oxide, and, therefore, must have been nitrogen. It was then apparent that an observed absorption of three moles of gas per mole of pentaphenylethane actually corresponded to an over-all reaction involving four moles of nitric oxide accompanied by the simultaneous liberation of one mole of nitrogen. Since the reaction has been shown to be strictly first order when calculated for an absorption of three moles of gas, both the primary reaction of the organic radicals with nitric oxide and the subsequent liberation of nitrogen

must take place at rates greatly exceeding the rate of dissociation of pentaphenylethane for they had no effect on the over-all rate when the initial nitric oxide pressure was one atmosphere.¹⁰

In order to identify the organic reaction products the reaction was carried out using larger quantities of pentaphenylethane but otherwise duplicating the conditions used in the rate measurements. Removal of the solvent left a partially crystalline residue from which triphenylcarbinol was isolated in essentially quantitative yield. The remaining oil slowly and partially crystallized on standing, giving a 23% yield of dibenzohydril ether.

Since the absorption of four moles of nitric oxide, the liberation of one mole of nitrogen and the formation of one mole of triphenylcarbinol were all found to be quantitative the isolation of dibenzohydril ether fixed the oxidation state of the remaining nitrogen in the form of nitrous acid (Eq. 6). Accordingly a search was made by

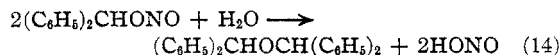
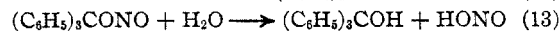
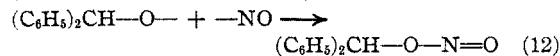
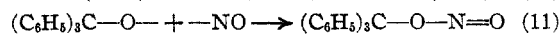
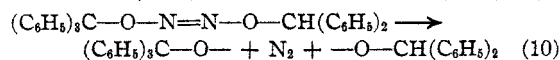
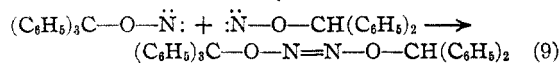
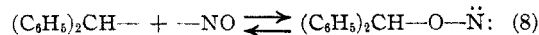
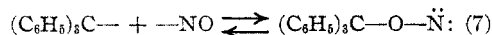


extracting the organic solution with dilute alkali immediately after a run. Nitrous acid was identified by conversion to diazoaminobenzene with aniline (27% of theoretical) and determined with standard potassium permanganate (33% of theoretical). We may regard Eq. 6 as a quantitative representation of the over-all reaction; the low yields of nitrous acid and of dibenzohydril ether may be attributed to the instability of the inorganic acid and to the ease of oxidation of the benzohydril group during the isolation of the organic products. Indeed, we have been able to isolate benzophenone, as the 2,4-dinitrophenylhydrazones, in 10% yield from the reaction mixture.

Shortly after we began this investigation a paper by Nauta and Mulder appeared which is in excellent agreement with our observations.¹¹ These authors studied the action of "molecular" silver on diphenylchloromethane in a nitric oxide atmosphere. Since it has been shown that mercury reacts with diphenylbromomethane to give the diphenylmethyl radical^{8b} they were undoubt-

edly studying the action of nitric oxide on this radical. They reported the evolution of an indefinite amount of nitrogen during the reaction and isolated a 75% yield of dibenzohydril ether together with a 4% yield of benzophenone. They found no organic reaction products containing nitrogen. It appears, then, that the action of nitric oxide on the diphenylmethyl radical is essentially the same at room temperature and at 100° and is independent of the radical forming reaction. We do not concur in the mechanism proposed by Nauta and Mulder for the reaction although we agree that the diphenylmethoxy radical must be an intermediate (*vide infra*).

Mechanism for the Reaction.—The series of reactions represented by Eqs. 5 and 7–14 constitutes a plausible mechanism which is consistent with all of the experimental data obtained in this investigation and with the established properties of analogous compounds. The primary and rate controlling step has been shown to be the dissociation of pentaphenylethane into free radicals (Eq. 5). The nitric oxide reacts with the resulting triphenylmethyl and diphenylmethyl radicals giving triphenylnitroxylmethane and diphenylnitroxylmethane, respectively (Eqs. 7, 8). These nitroxylmethane derivatives rapidly associate giving an organic ester of hyponitrous acid (Eq. 9). The dialkyl hyponitrite rapidly breaks down into nitrogen and alkoxy radicals (Eq. 10)



which react with nitric oxide to give stable esters of nitrous acid (Eqs. 11, 12). These esters are hydrolyzed by moisture giving the carbinol and the carbinol ether, respectively (Eqs. 13, 14).

Discussion of the Mechanism (Equations 7, 8).

—The postulation of an organic compound having the structure $\text{R}-\text{O}-\dot{\text{N}}$ is without parallel in so far as we have been able to ascertain. The parent inorganic compound, nitroxyl, $\text{H}-\text{O}-\dot{\text{N}}$; however, has been reported as an extremely re-

(10) The liberation of nitrogen in the reaction means, of course, that the partial pressure of nitric oxide was continually decreasing during a run. This provides additional evidence that the rate controlling step, at one atmosphere pressure, is independent of the nitric oxide pressure. The gas capacity of the reaction flask was such that the pressure decrease was approximately 0.1 atmosphere.

(11) Nauta and Mulder, *Rec. trav. chim.*, **58**, 1070 (1929).

active substance readily dimerizing to hyponitrous acid.¹² Moreover, there are several objections to postulating the isomeric nitrosomethane derivatives as intermediates.

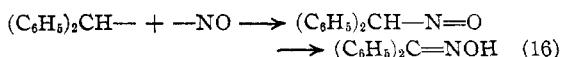
Schlenk and Mair studied the absorption of nitric oxide by ether solutions of triphenylmethyl at room temperature.¹³ Reaction was rapid and the yellow color of the radicals quickly changed to the blue-green color of triphenylnitrosomethane (Eq. 15).



The color was transitory, however, and neither the nitroso compound nor its colorless dimer could be isolated; instead concentration of the solution reversed the reaction giving back nitric oxide and triphenylmethyl.

Confirmation for the instability of triphenylnitrosomethane was reported by Ziegler, Orth and Weber, who investigated nitric oxide as a reagent for measuring the rate of dissociation of hexaphenylethane at 0°. They found that the reaction was not first order and the quantity of nitric oxide absorbed greatly exceeded one mole per triphenylmethyl radical. The addition of aniline, which presumably reacted irreversibly with the triphenylnitrosomethane, gave a first order reaction and made possible an accurate determination of the rate constant even though the reaction required nearly three moles of gas per triphenylmethyl radical. Despite a promise by the authors, no mechanism for this reaction has yet appeared.

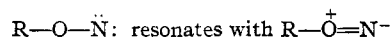
The formation of diphenylnitrosomethane from nitric oxide and diphenylmethyl would be expected to give benzophenone oxime (Eq. 16), in accordance with the known instability of second-



ary nitroso compounds. We were not only unable to isolate any benzophenone oxime from the reaction between nitric oxide and pentaphenylethane but in parallel experiments to which we added known quantities we were able to achieve almost quantitative recovery. Since benzophenone oxime is stable under the reaction conditions it seems likely that diphenylnitrosomethane was never formed.

Since the formation of triphenylnitrosomethane is at least partially reversible even at 0° and

since diphenylnitrosomethane is a most unlikely reaction product, we have rejected these compounds as possible intermediates in the reaction sequence. The most obvious alternative is the formation of nitroxylmethane derivatives postulated in Eqs. 7 and 8. To be sure, the formulas contain a neutral nitrogen atom with but six "valence" electrons; actually the compounds are stabilized by resonance with a form in which the nitrogen has an octet of electrons and a formal negative charge. Despite this stabilization these nitroxyl derivatives must be highly



unstable and would be expected to undergo rapid dissociation into their component radicals.

Equation 9.—The union of two nitroxylmethane derivatives to give a hyponitrous ester is highly probable from an energetic standpoint; moreover, the parent inorganic compound is reported to undergo such a reaction.¹² The dimerization, however, necessitates the coupling of two substances which in themselves are unstable and must be present in extremely small concentration. Nevertheless, we have qualitative evidence for this step in the reaction sequence through a rather fortunate set of circumstances.

We have found that at low nitric oxide pressures the over-all reaction rate becomes a function of the nitric oxide pressure. It is evident that under these conditions some reaction involving nitric oxide becomes the rate controlling step. Since the direct attack of nitric oxide on pentaphenylethane has been precluded even at higher pressures this rate controlling step at low pressures must involve the removal of the organic radicals.

At higher temperatures, with consequently faster dissociation of pentaphenylethane, correspondingly higher pressures of nitric oxide are required in order that the over-all reaction rate be not limited by the radical capturing reactions. At 105°, the highest temperature studied, the absorption was still accurately three moles per mole of pentaphenylethane when the partial pressure of nitric oxide was one atmosphere and the rate constant coincided with that calculated from the $-\log k$ versus $1/T$ plot used to obtain the activation energy (Fig. 3). We have concluded, therefore, that at 105° and one atmosphere pressure the rate-controlling step is the dissociation of pentaphenylethane. When the par-

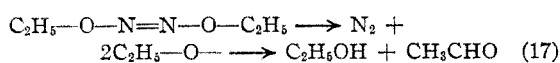
(12) "Gmelins Handbuch der anorganischen Chemie," 8th edition, Verlag Chemie, Berlin, 1936, System-Nummer 4, p. 855.

(13) Schlenk and Mair, *Ber.*, **44**, 1169 (1911).

tial pressure of nitric oxide was decreased to 0.5 atmosphere, however, the "rate constant," calculated from the slope at the beginning of the run, dropped to less than one-third of the dissociation rate constant although the total absorption decreased by only 10%. This superproportional effect of nitric oxide pressure on rate cannot be attributed to the reactions represented by Eqs. 7 and 8. These reactions are bimolecular and the rate of such reactions could only be proportional to the nitric oxide pressure. If, however, the reaction represented by Eq. 9 became the rate-controlling step at low nitric oxide pressures, and if reactions 7 and 8 were relatively rapid and reversible, then the over-all reaction rate would be proportional to the square of the nitric oxide pressure which is in qualitative agreement with our experiments at 105°.

Equation 9 represents the formation of triphenylmethyldiphenylmethyl hyponitrite, an unsymmetrical ester. Equally satisfactory, of course, would be the association of similar nitroxylmethane derivatives to give symmetrical hyponitrites.

Equation 10.—The postulated decomposition of triphenylmethyldiphenylmethyl hyponitrite into nitrogen, triphenylmethoxy and diphenylmethoxy radicals is in accord with the established properties of hyponitrous esters. Thus, ethyl hyponitrite decomposes rapidly in the presence of water at 40° giving nitrogen, ethanol and acetaldehyde (Eq. 17).¹⁴ The ethanol and acetalde-



hyde are disproportionation products of the intermediary ethoxy radical.

Spielman recently attempted the synthesis of triphenylmethyl hyponitrite from triphenylmethyl chloride and silver hyponitrite.¹⁵ He was not able to isolate the ester for the solution rapidly decomposed giving nitrogen and a variety of organic products. The secondary reaction products which were isolated, however, were easily explained by assuming an intermediate triphenylmethoxy radical.

Equations 11, 12.—The triphenylmethoxy and diphenylmethoxy radicals resulting from the decomposition of the hyponitrous ester would be expected to react with the free radical present in

largest concentration, *i. e.*, nitric oxide. The resulting nitrites should be stable in dilute solution. Although we have found no analogy for this reaction a reverse reaction, the thermal decomposition of ethyl nitrite at 200°, is homogeneous and unimolecular and the products, nitric oxide, ethanol and acetaldehyde indicate a primary decomposition into nitric oxide and ethoxy radicals.¹⁴

Equations 13, 14.—We were unable to isolate the triphenylmethyl- or diphenylmethyl nitrite, obtaining instead their hydrolysis products. That these nitrite esters are easily decomposed was confirmed by treating triphenylbromomethane and diphenylbromomethane with silver nitrite under conditions similar to those obtaining in the reaction between nitric oxide and pentaphenylethane. The yields of triphenylcarbinol and dibenzohydril ether were 94 and 60%, respectively.

Experimental

Most of the absorption and all of the rate measurements were carried out in an air thermostat described by Cain and Wiselogle.⁶ The procedure differed from their description in only two particulars. Solid pentaphenylethane is stable at 100°; hence there was no need for haste in beginning the rate measurements; the theoretical absorption, V , was calculated from the weight of pentaphenylethane taken, w , using the equation: $V = 455.7w(t + 273)/P$, where P is the barometric pressure and t is the buret temperature. The quantity of pentaphenylethane taken was usually 0.4 g., the amount of solvent determining the concentration.

Identification of Nitrogen as a Reaction Product.—At the conclusion of a normal rate run, the rubber tubing leading from the reaction flask was tightly constricted with a screw clamp. The tube was then cut off above the clamp and the open end was attached to the stem of an upright funnel of 12.7-cm. diameter filled with dilute acidified potassium permanganate solution. The stem of the funnel was extended upward about 5.1 cm. by the insertion of a tightly fitting glass tube. A buret was inverted and the open, flared end was dipped in the permanganate solution over the funnel stem. By applying suction at the tip the buret was filled with the solution. When the screw clamp was removed the gases in the flask escaped through the funnel stem into the buret and the volume of the residual nitrogen was measured. Blank runs were made on each sample of nitric oxide used and the appropriate correction made. The volume of gas was converted to moles by correcting for the difference in height of the liquid in the buret and in the funnel, the aqueous tension of the solution, temperature and atmospheric pressure. In three experiments the residual gas was found to be 1.08, 1.16 and 0.88 moles per mole of pentaphenylethane.

Isolation of the Organic Reaction Products.—In a 1-liter 3-necked balloon flask provided with a mercury-sealed stirrer were placed 8.20 g. of pentaphenylethane and 58.8 g. of *o*-dichlorobenzene. The air in the system was succes-

(14) Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, New York City, N. Y., 1937, pp. 1-2.

(15) Spielman, *THIS JOURNAL*, **57**, 1117 (1935).

sively displaced by dry nitrogen and nitric oxide; the outlet was then closed and the inlet was connected, through a drying train, to a reservoir of nitric oxide maintained at atmospheric pressure. The flask was warmed to 98° for one and three-fourths hours, while the contents were stirred, and then cooled to room temperature. After displacing all of the nitric oxide by nitrogen the solution was transferred to a distilling flask and the solvent was removed under reduced pressure at 100°. The residue, weighing 9.6 g., was treated with 50 cc. of 30–60° petroleum ether which precipitated the triphenylcarbinol. On filtering, 5.275 g. of product melting at 142–157° was obtained (theoretical yield 5.200 g.). Recrystallization from petroleum ether raised the melting point to 162–163° and the melting point of a mixture with triphenylcarbinol showed no depression. Reduction of the product with formic acid gave triphenylmethane which was also characterized.

Removal of the petroleum ether from the filtrate left an oil which slowly and only partially crystallized. A total of 0.815 g. of product melting at 109–110° was obtained, corresponding to a yield of 23.3%. The product was identified as dibenzohydril ether by comparison with a sample prepared from benzohydrol and copper.¹⁶

The distillate was examined for any possible nitration product by refluxing with 25 g. of tin and 40 cc. of concentrated hydrochloric acid over a period of six hours. The aqueous fraction was made alkaline and extracted with ether; evaporation of the ether gave a negligible residue indicating the absence of any amine and therefore the absence of any volatile nitration product in the original reaction mixture.

In a search for benzophenone, one of the reaction runs used to determine the rate constant was used. The residual oil, after removal of the solvent and crystalline triphenylcarbinol, was dissolved in 15 drops of ethanol and treated with 0.1 g. of 2,4-dinitrophenylhydrazine. The addition of 1 drop of concentrated hydrochloric acid gave a precipitate which was identified as the 2,4-dinitrophenylhydrazone of benzophenone. The quantity isolated corresponded to a 10% yield of benzophenone.

Cryer has shown that benzophenone oxime may be quantitatively extracted from organic solvents with 10% sodium hydroxide solution.¹⁷ In order to demonstrate the absence of benzophenone oxime as one of our reaction products, we treated the solution from a rate determination with 10% alkali. When the aqueous extract was acidified, however, only a faint opalescence was observed. Moreover, in a parallel experiment to which benzophenone oxime was added, we were able to achieve almost quantitative recovery. Failure to isolate benzophenone oxime, therefore, proves that it is not a significant reaction product.

Identification and Determination of Nitrous Acid.—In a reflux apparatus provided with a mercury-sealed stirrer and ground glass connections were placed 0.500 g. of pentaphenylethane and 25 cc. of *o*-dichlorobenzene. The air in the apparatus was successively displaced by nitrogen and by nitric oxide and the mixture was heated at 100°

with stirring for thirty minutes in a nitric oxide atmosphere. The nitric oxide was displaced by nitrogen and the cooled solution was transferred to a separatory funnel and agitated with 20 cc. of 0.2 *N* sodium hydroxide solution. The aqueous extract was cooled to 0° and acidified with 1.0 cc. of concentrated hydrochloric acid. To the acid solution was then added 0.453 g. of aniline and after a few minutes 0.50 g. of anhydrous sodium acetate. After standing for thirty minutes the precipitated diazoaminobenzene was filtered and washed with water. The product weighed 0.130 g., corresponding to a 27% yield of nitrous acid, and melted with decomposition at 92–94°.

In a similar experiment the alkaline extract was agitated with 5 cc. of benzene to facilitate separation of the aqueous and organic layers. The aqueous solution was then drained into a flask containing an excess of 0.1 *N* potassium permanganate solution, the solution was acidified, warmed and the excess titrated with standard ferrous sulfate.¹⁸ A blank was run by heating 25 cc. of solvent with nitric oxide for thirty minutes followed by titration of the alkaline extract. In two runs, correcting for the blank, the indicated yields of nitrous acid were 32 and 34%.

Action of Silver Nitrite on Alkyl Halides.—In a reflux apparatus provided with a mercury-sealed stirrer and ground glass connections were placed 1.75 g. of silver nitrite and 20 cc. of *o*-dichlorobenzene. When all of the air in the system had been displaced by nitrogen, a solution of 2.47 g. of diphenylbromomethane in 30 cc. of *o*-dichlorobenzene was added to the silver nitrite. The mixture was stirred for three hours at room temperature during which time some brown fumes were evolved, indicating some spontaneous decomposition of diphenylmethyl nitrite. The silver bromide and excess silver nitrite were filtered off and the solvent was removed under reduced pressure at 100°. The residual oil crystallized on standing. The crystals were washed with cold 30–60° petroleum ether, yielding 1.250 g. melting at 80–103°. Recrystallization from alcohol gave a total yield of 1.055 g. melting at 108–109.5°, corresponding to a 60% yield. The product was identified as dibenzohydril ether by comparison with an authentic sample.

In a similar experiment 3.23 g. of triphenylbromomethane, 1.58 g. of silver nitrite and 50 cc. of *o*-dichlorobenzene were stirred in a nitrogen atmosphere for two hours at room temperature and thirty minutes on a steam-bath. No brown fumes could be detected at any time. The triphenylcarbinol crystallized on removal of the solvent under reduced pressure at 100°. Washing the crystals with a little cold 30–60° petroleum ether yielded 2.45 g. (94%) melting at 162–163.5°. To ensure that a reaction between silver nitrite and triphenylbromomethane had taken place, the silver bromide was isolated by digestion of the inorganic precipitate with concentrated nitric acid, which dissolved all of the unreacted silver nitrite.

Summary

A study has been made of the kinetics and nature of the reaction between nitric oxide and pentaphenylethane at 90–105°. For nitric oxide pressures of one atmosphere the reaction is

(16) Knoevenagel and Heckel, *Ber.*, **36**, 2827 (1903).

(17) Cryer, Dissertation, "The Autocatalytic Decomposition of Benzophenone Oxime in Acetic Acid," University of Chicago, 1939.

(18) Scott, "Standard Methods of Chemical Analysis," 5th edition, D. Van Nostrand Co., New York, N. Y., 1939, p. 653.

stoichiometric and the rate controlling step is the unimolecular dissociation of pentaphenyl-ethane into free radicals. A four-step mechanism for the capture of the organic radicals by nitric oxide has been proposed. Since the overall reaction is quantitative and irreversible in the

absence of additives and since the fate of the radicals is known nitric oxide possesses unusual advantages as a reagent for studying the rates of dissociation of organic compounds at elevated temperatures.

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Mechanical Influence upon Tanning

BY JOHAN BJORKSTEN AND WILLIAM J. CHAMPION

The aldehyde content in human blood is so high,¹ that in the light of experience with industrial protein gels, it should amply suffice to tan the body proteins to complete rigidity and loss of elasticity within a matter of months. While such progressive tanning is evidenced by the loss of elasticity of tissues such as for example the arteries^{2,3} with aging, the rate of this tanning is much less than one would expect in view of the tanning substances present in body fluids.

Therefore, it appeared that this tanning might be retarded by factors not previously considered, and that a study of progressive tanning of protein gels during rhythmical motion simulating that of living arteries, might yield information bearing on this subject. The present investigation was made with this aim in view.

Since high Bloom gelatins are protein substances obtained by the mildest type of extraction, and since their behavior when tanned with slight amounts of tanning agents has been most thoroughly studied and understood,⁴ this protein was selected for our initial study.

300 grams of 225 Bloom pig skin gelatin was allowed to swell in a mixture of 300 g. of glycerol and 450 g. of water, at room temperature. After one hour, the mixture was melted in a water-bath of 55° and mixed with 1500 g. of additional glycerol, pre-warmed in the same water-bath.

The resultant mix was divided in two 50% aliquots. To one of these we added 60 cc. of 33% acetaldehyde solution, as tanning agent; the other aliquot served as our non-tanned control.

The mixes were allowed to stand one-half hour at 55°, to eliminate air bubbles, and were then poured to form uniform sheets having the dimensions 330 mm. × 210 mm. × 2.5 mm. Two such sheets were obtained from each aliquot.

The sheets were allowed to stand for twenty hours at room temperature, in order to give them the firmness required.

After this period, one tanned and one non-tanned sheet were attached with one short end to a rigid metal holder, and with the other short end to a holder having a reciprocating motion, so that the sheets were continually stretched and relaxed at a rate of eight times per minute, to an extent of 10% elongation.

The other two sheets, one tanned and one non-tanned, were placed on a porous backing next to the stretching machine, and were thus exposed to room temperatures, humidities and ventilation identical with those of the stretched samples.

After twelve days, the stretching was interrupted, the sheets were kept overnight (sixteen hours) at 55% relative humidity and 21°. Test strips were cut from center and ends of each sheet having their length parallel to the direction of stretch, and others perpendicular thereto, and the tensile strength was determined in a conventional paper tensile strength testing machine.

The tabulated figures are averages of triplicate determinations, all of which were within 5% of the averages shown.

TABLE I
TENSILE STRENGTH IN GRAMS PER SQ. MM.

		In direction of stretch	Across direction of stretch
Stretched	End	171	144
tanned sheet	Center	192	146
Stretched non-	End	153	148
tanned sheet	Center	150	152
Tanned non-stretched sheet		60	
Non-tanned non-stretched sheet		155	

With the stretched sheets, determinations were made at the end and the center of each sheet, as the direction of stretch might have shown slight deviations near the edges.

The most striking facts shown by these data are: (I) that the stretched tanned sheet not only is vastly stronger (320%) than the non-stretched tanned sheet in the direction of stretch, but also in the direction perpendicular to the tension

(1) K. Ri, *J. of Bioch., Tokyo*, **32**, 38-50 (1940).

(2) J. C. Bramwell, A. V. Hill and B. A. McSwiney, *Heart*, **10**, 233 (1923).

(3) J. M. Steele, "Abstracts of the Atlantic City Meeting of the American Chemical Society," September, 1941, p. B2.

(4) J. Bjorksten, *Chem. Ind.*, **48**, 749 (1941).