alkyl and alkyl–oxygen nonbonding interactions that are greater in the hydroxylamines and oximes than in the corresponding radicals, since the latter have a more open geometry. In addition, nonbonding interactions involving the hydrogen that is removed are eliminated.

These steric effects on the O–H bond strength should be at a maximum with di-*tert*-butyl nitroxide[23] in which the relevant CNC angle is 136° and the CNO angle is 112°. In the hydroxylamine, if the nitrogen is tetrahedral, the angles will be 108°. Unfortunately di-*tert*-butyl nitroxide reacted so slowly with hydrazobenzene in CCl_4 and in benzene that the heat of the reaction could not be determined. The slowness of reaction suggests that the O–H bond strength in this compound is several kcal/mole less than in **1**, since the sterically more hindered but thermoneutral hydrogen transfer from di-*tert*-butylhydroxylamine has a rate constant of over $10^2\ M^{-1}\ \text{sec}^{-1}$ in CCl_4 at room temperature.[31]

The importance of steric factors in determining the O–H bond strength in **1** is difficult to estimate. However, the six-membered ring should inhibit any large changes in the CNC angle on going from the hydroxylamine to the radical, so steric effects are probably small. It is interesting to note that the nitrogen hyperfine splitting for **1** in most solvents is similar to the values found for many less substituted and unstable, dialkyl nitroxides. In these radicals the alkyl groups are free to adopt a conformation minimizing steric interactions. We would accordingly predict that the O–H bond strengths in unhindered dialkylhydroxylamines are in the range 72–74 kcal/mol.

Steric effects should be absent in the bicyclic nitroxides **3** and **4**.

Replacement of a methyl group in **2** by a hydrogen atom increases the O–H bond strength in the oximes by *ca.* 3.4 kcal/mol (see Table V). This change must be steric in origin and has been attributed[13] to greater alkyl–alkyl and alkyl–oxygen repulsions in **2H** compared with **2** than in *tert*-butyl isopropyl ketoxime compared with its iminoxy radical. It is unlikely that a change of similar magnitude would accompany the replacement of additional methyls. We therefore expect that simple unhindered oximes will have O–H bond strengths of about 86 kcal/mol.

Radical Stability. The widespread use of nitroxides as spin labels in biological systems[32] depends critically upon their stability under the conditions of study. Although the "intrinsic stability" of the nitroxide group is sometimes cited, the very concept of stability requires some reference point. Hindered nitroxides of the kind used as spin labels have no kinetically feasible pathways for decomposition. Steric hindrance must be directly responsible for the lack of dimerization of **1** and of di-*tert*-butyl nitroxide since the less hindered radicals **3** and **4** dimerize reversibly.[12,33] The low O–H bond strength of hydroxylamines means that hydrogen abstraction from most organic substrates by the nitroxide will be a highly endothermic, and hence slow, process. Other potential reactions, such as addition to the terminii of double bonds, are even more strongly retarded than hydrogen abstractions because nonbonding repulsions in the product will be even greater than in the hydroxylamine.

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(31) R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **88**, 2645 (1966).

(32) For leading references, see W. L. Hubbell and H. M. McConnell, *J. Amer. Chem. Soc.*, **93**, 314 (1971).

(33) Nitroxides **1**[34] and **3**[12] also undergo slow irreversible dimerization.

(34) Y. Takeo, S. Morimura, and K. Murayama, *Bull. Chem. Soc. Jap.*, **44**, 2207 (1971).

Flash Photolytic Decomposition of Aryl Azides. Measurement of an Intramolecular Closure Rate

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Abstract: We have studied the formation of carbazole from flash photolysis of 1-azidobiphenyl. The reaction proceeds through the formation of 2-nitrenobiphenyl. The first-order rate coefficient at 300°K is $2.18 \times 10^3\ \text{sec}^{-1}$ and ΔH of activation is 11.46 kcal/mol (± 0.76) in cyclohexane solution. These quantities were measured from the rate of appearance of carbazole and confirmed by the rate of disappearance of the nitrene, in ultraviolet absorption spectra. The reaction in the gas phase was too fast for us to measure; a lower limit for the rate constant in the gas, at 75°, is $1.4 \times 10^6\ \text{sec}^{-1}$. The mechanism in solution is inferred to be an addition of nitrene to the neighboring phenyl ring, followed by hydrogen migration. Together with the evidence presented by Swenton, Ikeler, and Williams, our results imply that both singlet and triplet states of the nitrene are involved in carbazole formation, in that sequence. We also report the confirmation of the gas-phase near-ultraviolet spectrum of phenyl nitrene and the measurement of the rate coefficient for the reaction $C_6H_5N + C_6H_5N_3 \rightarrow C_6H_5N{=}N\,C_6H_5 + N_2$, the observation of the near-ultraviolet absorption spectrum of 1-naphthyl nitrene, and the observation of the formation, in the gas phase, of the dimer of 2-nitrenodiphenylmethane from photolysis of 2-azidodiphenylmethane.

The decomposition reaction of 2-azidobiphenyl has been well studied. In solution, excited either photochemically or thermally, the reaction proceeds smoothly to give carbazole in high yield.[2,3] In fact, the yield is sufficiently high to allow the use of the reaction as a synthetic pathway to various substituted

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(1) Fannie and John Hertz Foundation Fellow.

(2) (a) P. A. S. Smith and B. B. Brown, *J. Amer. Chem. Soc.*, **73**, 2435 (1951); (b) *ibid.*, **73**, 2438 (1951).

(3) J. S. Swenton, T. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, **92**, 3103 (1970).

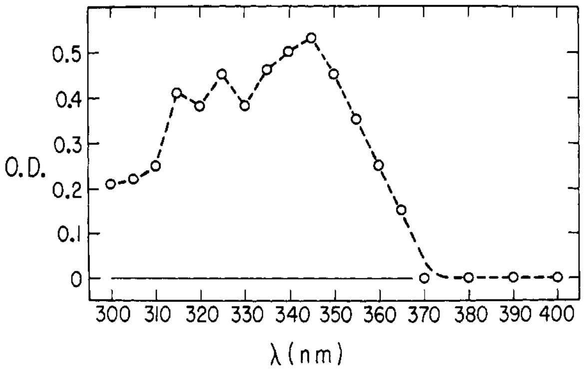
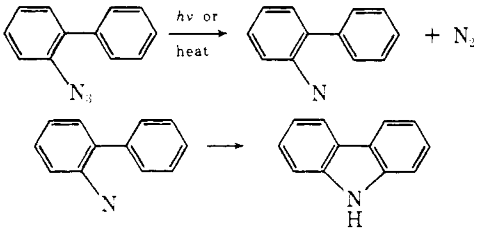


Figure 1. Absorption spectrum of 2-nitrenobiphenyl, taken 50 μsec after photolysis of 2-azidobiphenyl in cyclohexane. Units are optical density, to base 10.

carbazoles.[2] The photolytic decomposition has also been studied at 77°K in an EPA glass and was shown to proceed through a single photochemical intermediate, again to produce carbazole in high yield.[4] The intermediate was tentatively identified as the nitrene by its uv spectrum which was similar to the spectrum of the isoelectronic benzyl radical and also to spectra of other intermediates produced by corresponding azide photolyses.[5] The crude microscopic picture of the reaction that has emerged from these studies is



(1)

(2)

The azide first loses molecular nitrogen to form the nitrene which subsequently reacts (in some as yet unspecified way) to form carbazole. By using the technique of flash photolysis to prepare a relatively large concentration of the intermediate nitrene in a short time, we have been able to measure the rate of the intramolecular closure reaction (reaction 2) and its activation energy. Using these measurements and other considerations, we have also postulated a reasonable mechanism by which the closure takes place.

Results

Although measurements of the closure rate were made both in solution and in the gas phase, the solution measurements were by far the more complete. They consisted of 11 measurements of the reaction rate at temperatures ranging from 288.6 to 319.1°K in cyclohexane solution at a concentration of the starting azide of 6.67×10^{-6} M.[6] The rates were measured by monitoring the carbazole concentration spectrophotometrically at 2894 Å, a wavelength at which carbazole absorbs strongly. The more obvious and direct method for the measurements, that of monitoring the intermediate nitrene concentration, was not suitable for accurate measurements. A combination of experimental limitations, the relatively low extinction coefficient of the nitrene absorption, and interference from overlapping carbazole absorptions served to make this direct method very difficult. However, a semiquantitative measurement of the nitrene decay rate was possible, and the measured rate was found to agree with the carbazole formation rate, at least to within a factor of 2.

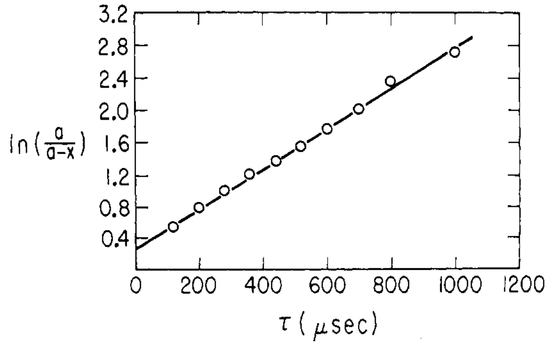


Figure 2. First-order rate plot for carbazole formation in cyclohexane at 340.0°K.

In addition, the nitrene was identified flash spectroscopically. A spectrum of the sample taken 50 μsec after photolysis is in excellent agreement with the spectrum attributed to the nitrene in an EPA matrix.[4] This spectrum is shown in Figure 1. Both the nitrene absorption of 3420 Å and the beginnings of the carbazole absorption at 3250 and 3150 Å are evident. In addition, the percentage conversion of 2-azidobiphenyl to carbazole in a single flash was measured spectroscopically to be 78%. These experiments showed that the nitrene is present as an intermediate and that no important side reactions interfere with the reaction of interest. Thus, the measurement of the carbazole concentration is an accurate reflection of the rate of the intramolecular closure.

The rate of reaction at each temperature was determined in the following way. From a Polaroid picture showing the light intensity passing through the sample as a function of time, the carbazole concentration as a function of time was calculated. With the assumption that each product carbazole molecule arises unimolecularly from an intermediate nitrene molecule, the decomposition of the nitrene was fitted to a first-order kinetic scheme and yielded a straight line at each temperature. An attempt to fit the data to second-order kinetics was unsuccessful. The slope of the first-order rate plot, and thus the rate constant for the closure reaction, was determined by the method of weighted least squares.[7] Each concentration measurement in the plot was weighted by the square of the concentration of the unreacted nitrene, as calculated by the amount of carbazole that was formed. This gives relatively more weight to concentration measurements early in the reaction when relatively large changes in concentration are taking place and when the accuracy of the measurement is greater. The reactions were generally followed for 3–4 half-lives. Figure 2 shows a typical first-order plot obtained in this way.

Table I gives the results of all the rate measurements. The probable errors (or 50% confidence limit) were

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(4) A. Reiser, H. Wagner, and G. Bowes, *Tetrahedron Lett.*, **23**, 2635 (1966).

(5) A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

(6) Experiments were performed to ascertain that cyclohexane does not participate in the reaction *via* a hydrogen abstraction by the nitrene. It was found to be inert.

(7) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," Wiley, New York, N. Y., 1943, pp 238–243.

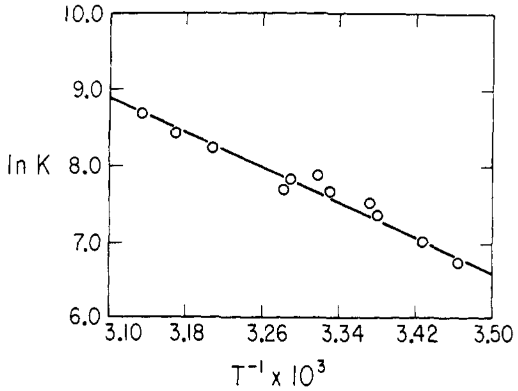

Figure 3. Arrhenius plot yielding activation energy of 11.46 ± 0.76 kcal/mol for the formation of carbazole in cyclohexane solution.

Table I. Rates, Half-Lives, Probable Error, and Relative Weights for the Arrhenius Plot for the Photolysis of 2-Azidobiphenyl in Cyclohexane Solution

Temp, °K	Rate $\times 10^{-3}$, sec^{-1}	Half-life, μsec	Probable error $\times 10^{-3}$, sec^{-1}	Rel wt
319.1	5.84	119	0.192	0.052
315.6	4.59	151	0.124	0.081
311.7	3.79	183	0.125	0.080
304.7	2.15	322	0.035	0.283
304.0	2.53	274	0.063	0.158
301.4	2.65	262	0.071	0.141
300.3	2.18	318	0.066	0.151
296.6	1.85	376	0.032	0.314
295.8	1.56	444	0.121	0.083
291.7	1.11	624	0.332	0.316
288.6	0.86	806	0.011	0.943

calculated in the usual way.[7] The reciprocal of the probable error of each rate constant was used to weight each point for the Arrhenius plot of ln k *vs.* $1/T$. This gives relatively more weight to those rate constants which have been more accurately measured and is the suggested method.[8] The slope of the Arrhenius plot shown in Figure 3 was then also calculated by the method of weighted least squares. The calculation yields an activation energy for the overall reaction of 2-nitrenobiphenyl to carbazole of 11.46 kcal/mol with a probable error of ±0.76 kcal/mole.

Attempts to extend the solution work to the gas phase were only partly successful. The reaction was first studied by flash spectroscopy. A sufficient vapor density of starting material was achieved by heating the sample cell containing a small amount (1–2 mg) of solid azide to *ca.* 75°. Perfluoroethane, at a pressure of 400 Torr, was used as a diluent gas, assuring isothermal conditions by limiting the temperature rise to less than 1° when the gases in the cell reached thermal equilibrium among themselves. The experiments show that carbazole is again the only product, but unfortunately, under these conditions, the closure reaction occurs faster than the time resolution of the method. By various experimental modifications, the time resolution was improved to ±1 μsec, but the reaction still occurred faster than could be detected. This sets an upper limit of about 0.5 μsec for the half-life of the reaction, and thus a lower limit of about 1.4×10^6 sec^{-1} for the rate constant. Of course, the shortness of the half-life prevented any observation of the nitrene in the gas phase.

Discussion

From the data just described it is possible to formulate a detailed mechanism for the reaction. Before doing so, however, it is important to point out that the mechanism of the gas phase reaction is not necessarily the same as that of the solution reaction. A simple extrapolation of the Arrhenius plot shows that the predicted rate constant for the gas phase reaction, if it were to occur by the same mechanism as the solution reaction, would be about 2.5×10^4 sec^{-1}. This is much smaller than the lower limit of the measured rate constant. Thus, the mechanisms may well be different. The implications of this difference will be discussed in detail below, but first, the mechanism in solution will be considered.

A useful clue in elucidating the mechanism is the spin state of the reacting nitrene. When the starting azide absorbs a photon and photodissociates, the two products formed are the nitrene and molecular nitrogen. Since N_2 has no excited electronic states of low enough energy to be populated by the reaction, it is necessarily formed as a ground-state singlet. Then, according to spin selection rules, the nitrene must also appear initially as a singlet. However, a singlet nitrene is not what is observed. As mentioned, the observed spectrum of the nitrene is in excellent agreement with the spectrum obtained at 77°K. Since the nitrene at 77°K is undoubtably in its ground state and since the ground state of similar nitrenes has been shown to be a triplet by esr spectroscopy,[9] we can confidently assign the observed nitrene as a triplet. Thus, the first step (following loss of N_2) in the mechanism must be the fast intersystem crossing by the singlet nitrene to its triplet ground state.

The next step in the mechanism is the formation of some sort of bond between the nitrogen atom and the neighboring phenyl ring. Although an *a priori* possibility for this bond formation is the direct insertion of the nitrene into the phenyl C–H bond, this possibility can now be ruled out because a singlet nitrene would be required for such a reaction. This leaves two other reasonable possibilities for the bond formation—either abstraction and recombination, or addition.

Since this bond formation is clearly the rate-determining step, the activation energy measured for the overall reaction is essentially the activation energy of this particular step. At this point, we may use the magnitude of the activation energy to help us choose between the addition mechanism and the abstraction mechanism. No data are available for activation energies of nitrene abstraction reactions, so it will be assumed in the following discussion that the triplet nitrene will behave much as an ordinary carbon radical.[10,11] No activation energies have been measured for abstraction of phenyl hydro-

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(8) S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill, New York, N. Y., 1960, pp 89–90.

(9) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3220 (1962).

(10) Since one of the unpaired electrons on the nitrogen atom of the triplet nitrene is in a p_z orbital and is thus delocalized into the π-electron cloud of the phenyl ring, while the other is in a nonbonding p_y orbital, the nitrene should react as if it possessed only one unpaired electron.

(11) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 155.

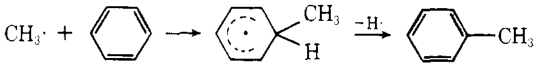
gens, even for carbon radicals, but data are available for hydrogen abstraction from methane and ethane by the methyl radical. The activation energies for the reactions

$$CH_3 + CH_4 \longrightarrow CH_4 + CH_3 \qquad (3)$$

$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad (4)$$

are 14.0 and 11.2 kcal/mol, respectively. The larger activation energy for abstraction from CH_4 reflects the greater bond dissociation energy of the C–H bond in CH_4 as opposed to C_2H_6. The CH_3–H dissociation energy is 104 kcal/mol while the C_2H_5–H dissociation energy is 98 kcal/mol.[12] The C_6H_6–H bond dissociation energy is 112 kcal/mol.[13] Let us assume that the trend exhibited by the methyl radical continues for the C_6H_5–H bond, *i.e.*, that almost half the difference in bond dissociation energies appears in the activation energy; then the activation energy for abstraction of a phenyl hydrogen by methyl is certainly greater than 14 kcal/mol, and probably about 17–18 kcal/mol. Because it can be assumed that the nitrene will behave similarly, this implies that the activation energy for the carbazole formation should be much higher than the 11.46 kcal/mole measured for the reaction, if the bond formation step proceeds by an abstraction–recombination mechanism. Hence the value of the activation energy suggests an addition mechanism.

There is further positive evidence in support of the addition mechanism. It is known that methyl and phenyl radicals react with benzene by addition rather than by abstraction. Two examples are[14]



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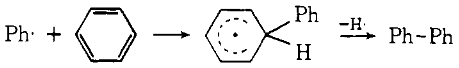
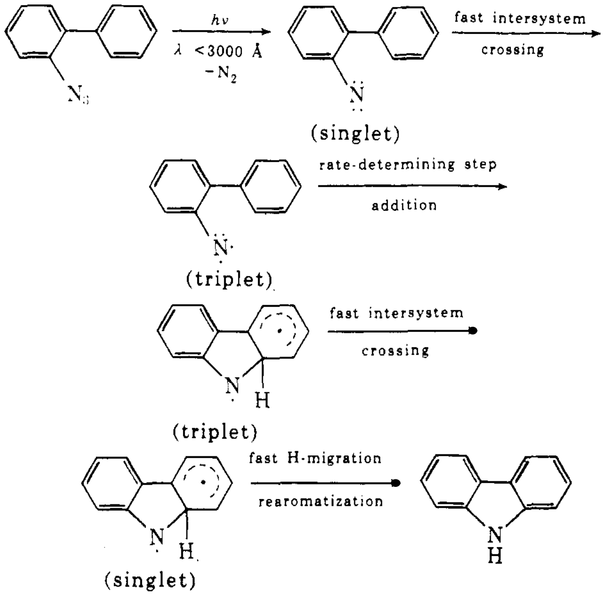


(6)

In the latter reaction, it is known that abstraction (as opposed to addition) is an unimportant side reaction. If we rely again on our assumption that the triplet nitrene will behave like a radical, this evidence suggests that the addition mechanism is the correct one.

The triplet intermediate formed in the rate-determining addition step will undergo intersystem crossing and become a singlet before the hydrogen migrates. We draw this inference as follows. Triplet carbazole would result if the hydrogen migrated before the electron spins were paired. The unpaired electrons in the triplet intermediate must be further apart than in triplet carbazole. Hence hydrogen migration should be a somewhat endothermic reaction if it occurred with the molecule in a triplet state. The intersystem crossing, on the other hand, should be a virtually thermoneutral reaction in the intermediate, since the electrons are only weakly correlated. Thus, the crossing presumably occurs first and is fast compared to the addition. After the spins pair, the hydrogen migration can occur easily. It is, in reality, an intramolecular hydrogen abstraction of a tertiary hydrogen by the nitrogen radical. Since tertiary hydrogens are substantially more reactive than primary or secondary hydrogens, and since the abstracting radical and the hydrogen atom are situated so close together, this reaction will certainly be fast. As the hydrogen migrates, the immense energy gained by rearomatization of the phenyl ring provides a large driving force and the subsequent pairing of electrons should also be fast.[15] The detailed mechanism that emerges from these arguments is



(7)

Thus, it is concluded that, in solution, the measurement of an activation energy of 11.46 kcal/mol for the carbazole formation is a measure of the activation energy of the addition of the nitrene to the neighboring phenyl ring, and that insertion and abstraction probably do not take place.

These results might appear at first to contradict the conclusions of Swenton, Ikeler, and Williams, who inferred that the singlet nitrene is the precursor of carbazole and that a triplet, either a nitrene or an azidobiphenyl, is a precursor of the azo dimer of the biphenyl nitrene. In fact, their results and ours are consistent and, taken together, lend some support to the case that the azo dimer is the product of the reaction of a triplet azide, not a triplet nitrene. The experiments of Swenton, Ikeler, and Williams show that direct photolysis and photosensitization with molecules in excited singlets favor carbazole formation, implying that a singlet excited state, either an azide or a nitrene, occurs in this reaction sequence. Our own results imply that a singlet nitrene is formed by photolysis, but that the singlet nitrene undergoes fast intersystem crossing, as in (7), and that the nitrene reacts to form a five-membered ring when it is a triplet; this is clearly the implication of our spectroscopic observations. Together, our results and those of Swenton, Ikeler, and Williams imply that *both* the singlet and triplet states of the nitrene occur along the pathways leading to a large fraction of carbazole. This conclusion, in turn, implies that the

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[12] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[13] A. S. Rodgers, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **89**, 4578 (1967).

[14] Reference 11, pp 224, 256–258.

[15] Note that in this paragraph we have tried to infer the sequence of these final steps in the mechanism on the basis of heats of reaction. Although heats of reaction generally need have no bearing on kinetics, in this case they probably have some relevance. The only particles moving in these final steps are electrons and a proton; hence the classical activation energy considerations used frequently to determine relative rates are inadequate, due to the ease with which these light particles can tunnel through an activation energy barrier. Thus, the light masses tend to reduce the effects of potential barriers and the speed of each step (and thus the sequence of the steps) is determined mainly by the heat of reaction.

triplet-sensitized process studied by Swenton, Ikeler, and Williams goes predominantly through a triplet state of the azide, rather than of the nitrene, which is one of the two alternatives proposed by Swenton, Ikeler, and Williams.

One other variant must be admitted as an alternative to (7), namely that the closure and T → S intersystem crossing are essentially simultaneous and associated with thermal activation to a singlet potential surface. The activation energy of 11.46 kcal/mol is certainly consistent with some singlet–triplet separations of heteroaromatic systems.

Things are not as clear-cut in the gas phase. Since vibrational quenching is not nearly as fast in the gas phase as it is in solution, there is some probability that the nitrene will react in the gas phase while it is vibrationally hot. In the foregoing discussion of the mechanism in solution, we have made the implicit (and reasonable) assumption that the reacting nitrene is in its ground vibrational state. Unless this is true, arguments about the magnitude of the activation energy are meaningless. In the gas phase, if we judge from the wavelengths of the threshold and the peak of the 2-azidobiphenyl absorption band, the nitrene might possess up to 25 kcal/mol in excess vibrational energy. This highly excited intermediate might well be a very reactive species, so reactive that even abstracting a phenyl hydrogen would have a low activation energy. Vibrational excitation is consistent with the high rate of the reaction in the gas phase, but it says nothing about the mechanism. It is impossible to choose between abstraction–recombination and addition (and perhaps insertion also, depending on the intersystem crossing rate), and probably both occur. The gas-phase reaction might perhaps involve the singlet nitrene. All that can be said about the reaction in the gas phase is that the product is the same as in solution, but that the microscopic description of the reaction is a mystery.

Gaseous Aryl Nitrenes

Photolytic decomposition of various aromatic nitrogen compounds is known to give aryl nitrenes in glasses and solutions,[4,5,16–19] and, in the two cases of *o*-chloroaniline and phenyl isocyanate, in gases.[20] We wish to report the observation of gaseous phenyl nitrene and 1-naphthyl nitrene prepared by flash photolysis of the corresponding azides, and the inference that gaseous 2-nitrenodiphenylmethane also exists.

Phenyl Nitrene. The near-ultraviolet spectrum of phenyl nitrene in the gas phase is reported to consist of one very sharp band at 368.3 nm, and a number of weaker bands between 370.7 and 345.3 nm.[20] The spectrum in an EPA glass at 77°K shows a broad peak in the region 330–400 nm, with a peak in the vicinity of 370 nm.[4] Flash photolysis of phenyl azide vapor alone, at its equilibrium vapor pressure at room temperature, shows only the strong, well-known absorption bands of CN, and no indication of phenyl nitrene. The CN probably arises in the following manner. When phenyl azide is photolyzed neat, the temperature rise in the cell due to the exothermicity of the reaction and to the photons absorbed is quite high, probably about 1000°.[21] Since it has been shown[22] that phenyl nitrene isomerizes to a cyclopentadienyl nitrile at temperatures about 550° the phenyl nitrene formed in the neat photolysis will also isomerize to the nitrile. The nitrile is then fragmented by the high thermal energies, and due to the strength of the C≡N bond, CN is a likely fragment. However, when sufficient inert quenching gas (perfluoroethane in our work) is added to maintain essentially isothermal conditions, the absorption band at 368.3 nm reported by Porter and Ward[20] appears. The identification of this band from phenyl azide photolysis seems to provide as definitive a confirmation of the assignment as medium-resolution spectroscopy can offer.

Due to the low intensity of the absorption, a 7-pass on-axis cell, patterned after that of Overend, *et al.*,[23] was used. The folded path has a length of 210 cm.

It was not possible to measure the rate of disappearance of phenyl nitrene directly, but the appearance of the only detected product, azobenzene, was monitored. The process exhibits pseudo-first-order kinetics. This, together with the observation that the yield of azobenzene is only about 6%, is a very strong indication that the reaction scheme is

$$C_6H_5N_3 + h\nu \longrightarrow C_6H_5N + N_2$$

$$C_6H_5N + C_6H_5N_3 \longrightarrow C_6H_5N{=}NC_6H_5 + N_2$$

The pseudo-first-order rate constant under nearly isothermal conditions ($T = 298 \pm 10$°K) is $5.0 \pm 1.0 \times 10^4$ sec^{-1}, when the initial partial pressure of phenyl azide is its equilibrium vapor pressure at about 298°K. This vapor pressure is not known, but is of order 1 Torr; if it were 1 Torr, the second-order rate constant would be about 1.3×10^{-12} cm^3/sec. Hence the rate of reaction of phenyl nitrene with phenyl azide is very high. The rate is high enough that quite efficient photolysis would be required to make it possible to observe the direct dimerization of two phenyl nitrenes, for example.

One aspect of the kinetic analysis deserves mention. The data, as shown in Figure 4, can be interpreted in terms of one reaction with a pseudo-first-order rate constant of $5.88 \pm 0.18 \times 10^4$ sec^{-1}, preceded by a slower reaction which also appears to satisfy first-order kinetics, over the very short interval of 10 μsec, with a constant of $3.12 \pm 0.17 \times 10^4$ sec^{-1}. Although the precision of these measured rate constants is very good for any one run, the scatter of the entire set of experiments was much poorer; the full range of measured rate coefficients spanned a factor of 2. However, the phenomenon of two first-order reactions, with a faster second reaction following a slower first reaction after a short time, is constant from run to run. Whether this was due to some induction process was not determined.

1-Naphthyl Nitrene. The absorption spectrum of 1-naphthyl nitrene has been obtained in an EPA glass,[5] but the spectrum of the gaseous naphthyl nitrene has not previously been reported. The spectrum in the cold matrix exhibits maxima at 220, 300, 355, 370, 500, and 540 nm.

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(16) A. Reiser and V. Frazer, *Nature* (*London*), **208**, 682 (1965).

(17) A. Reiser, H. Wagner, R. Marley, and G. Bowes, *Trans. Faraday Soc.*, **63**, 2403 (1967).

(18) A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968).

(19) A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, **64**, 3265 (1968).

(20) G. Porter and B. Ward, *Proc. Roy. Soc.*, *Ser. A*, **303**, 139 (1968).

(21) P. A. Lehman, Doctoral Dissertation, University of Chicago, 1971. Details of the apparatus and procedures are given here.

(22) E. Hedaya, M. E. Kent, and D. W. McNeil, *Tetrahedron Lett.*, **30**, 3415 (1968).

(23) J. Overend, J. H. Schachtschneider, R. W. Rinehart, and B. Crawford, *Spectrochim. Acta*, 448 (1959).

Photolysis of the vapor of 1-naphthyl azide was carried out in a sample cell warmed, to temperatures as high as 100°, to create a sufficiently high vapor density. Photolysis of the neat azide led to spectra exhibiting CN but no nitrene, just as in the case of phenyl azide. When perfluoroethane was added, at a pressure of several hundred Torr, the CN bands no longer appeared in the spectrum. Rather we observed a double-peaked absorption with maxima at 353.5 and 370.0 nm in close correspondence with the spectrum reported for the nitrene in an EPA glass. An absorption at shorter wavelengths would have been obscured by unphotolyzed starting material, and the long-wavelength bands would have been too weak to be observed.

The spectra of both phenyl nitrene and 1-naphthyl nitrene correspond to the spectra measured in an EPA glass at 77°K. Since the nitrenes at 77°K are necessarily in their ground electronic state and since the ground state of phenyl and other related aromatic nitrenes has been shown to be a triplet by esr spectroscopy,[24] this identifies the observed nitrenes as triplets. However, in the primary photodissociation of the azide, energetics require that the N_2 be formed as a singlet, and thus spin selection rules require that the nitrene also be formed as a singlet. This implies that the intersystem crossing rate is at least as fast as the time resolution of the experiment or we would have observed the singlet. The time resolution is approximately the duration of the analysis flash or about 6 μsec (see Experimental Section). Thus, 6 μsec is an upper limit to the lifetimes of these two singlet nitrenes toward decay to the ground state triplet.

2-Nitrenodiphenylmethane and Its Dimer. Photolysis of 2-azidodiphenylmethane vapor was carried out with the hope that a detectable amount of dihydroacridine would be produced by internal closure of the six-membered heterocyclic ring, and that the kinetics of this closure could be studied in the same manner as the closure of diphenylnitrene to carbazole. Transient spectra of the vapor taken between 50 and 1000 μsec after photolysis show two weak bands in the region of 434 and 436 nm, which may be due to 2-nitrenodiphenylmethane. The principal product of photolysis is a very strong absorber, essentially opaque in very small quantities at wavelengths shorter than about 380 nm.

The principal product, which is responsible for the absorption in the near-ultraviolet, was isolated in small quantities by thin-layer chromatography. The product is the azo dimer of the 2-nitrenodiphenylmethane, probably formed by attack of a nitrene on a molecule of azidodiphenylmethane starting material.

The product was identified as follows. The high-resolution mass spectrum indicated an empirical formula of $C_{26}H_{22}N_2$ (calcd mass, 362.1782 amu; obsd mass of parent peak, 362.1766). Large fragments occurred with masses of 285.1435 and 180.0798 due to loss of C_7H_7 and $C_{14}H_{14}$. Table II gives the fragmentation pattern. The material forms bright orange crystals melting at 108–110°.

Comparisons were made with authentic samples of dihydroacridine, 2-aminodiphenylmethane, and azepino-[2,1-*a*]-11H-indole, which was suggested by the work of Krbechek and Takimoto.[25] No product of photolysis could be found that corresponded to any of these materials.

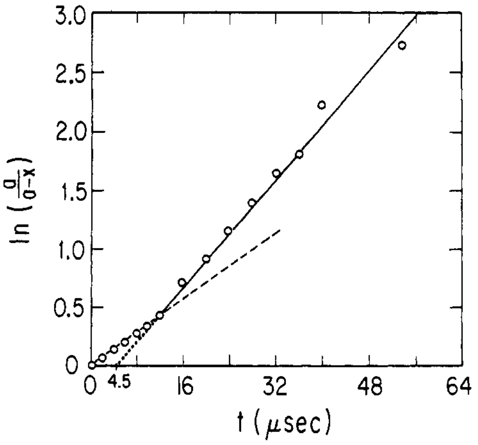

Figure 4. Pseudo-first-order rate plot for the formation of azobenzene from phenyl nitrene and phenyl azide. The concentration of azobenzene at time *t* is *x*; the initial concentration of phenylnitrene and the final concentration of azobenzene are given by *a*. The slope of the initial and flatter portion is 3.67 + 10^4 sec^{-1}; the slope of the longer and steeper portion is 4 × 10^4 sec^{-1}.

Table II. Mass Spectrum of 2,2′-Dibenzylazobenzene

Measured mass	Absolute intensity	% Int. Rel. N-Ref.
363.1771	2166	22.61
362.1766	9579	100
361.1702	6126	63.95
360.1605	1828	19.08
286.1430	1553	16.21
285.1435	8884	92.74
183.1048	3455	36.07
182.0979	1659	17.32
180.0798	4361	45.53
179.0728	929	9.70
167.0869	1822	19.02
166.0784	939	9.80
165.0715	4573	47.74
152.0628	1630	17.02
100.9984	2214	23.11
97.1044	1772	18.50
91.0555	1047	10.93
85.1025	2093	21.85
83.0876	2130	22.24
83.0828	1401	14.63
81.0683	1301	13.58
71.0825	2092	21.84
71.0756	1546	16.14

Experimental Section

The flash apparatus was set up for both flash spectroscopy and kinetic spectrophotometry in a fairly conventional manner.[21] The capacitor for the photolysis flash was a Tobe Deutschmann Model ESC-248A with a capacitance of 15 (μF), energy storage of 3000 J, and a low internal inductance cf 5 nH. The photolysis flash lamp was homemade, consisting of a quartz tube, 25 mm o.d., 19 mm i.d., and 25 cm long with a blunt stainless steel electrode sealed into each end with epoxy glue. One electrode was drilled through and fitted with a stopcock and a standard taper joint so the lamp could be evacuated and refilled. Argon, at pressure between 20 and 40 Torr, was the filling gas. The lamp was fired with a GE 7740 ignitron triggered by a conventional pulse circuit. The capacitor, lamp, and ignitron was connected by a parallel plate transmission line designed to minimize the inductance. The $e^{-1} \rightarrow e^{-1}$ flash duration of a 1000-J flash monitored at 3000 Å was 16 μsec.

For flash spectroscopic experiments, the background continuum necessary for absorption spectroscopy was provided by a second flash lamp. It consisted of a quartz capillary 7 mm o.d., 3 mm

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[24] G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, 84, 3220 (1962).

[25] L. Krbechek and H. Takimoto, *J. Org. Chem.*, 33, 4286 (1968).

i.d., and 3 cm long with an Elkonite electrode sealed at each end with an O-ring. A pinhole leak was continuously pumped to provide a pressure of about 5 Torr of air inside the lamp. A 4.5 μF, 20 kV capacitor supplied the energy for the flash which was also fired by a 7740 ignitron. The lamp was generally used at energies between 50 and 150 J. A 110-J flash monitored at 3000 Å had an $e^{-1} \rightarrow e^{-1}$ flash duration of 6 μsec. A light activated SCR sensed when the photolysis lamp fired and emitted a pulse which was appropriately delayed and then used to fire the analysis lamp. The absorption spectra were taken with a Hilger medium quartz spectrograph, on Kodak 103-0 and 103-F plates.

For kinetic spectrophotometric experiments, the background light was provided by an Osram 500-W, xenon–mercury arc lamp, Model HBO-500W, with a stability better than 2%. The desired wavelength was selected by passing the light through a Jarrell-Ash Model 82-410 monochromator after which it was detected by an EMI 6256S photomultiplier tube. A 3.2-Å bandpass was employed. An elaborate system of slits and baffles was necessary to prevent the scattered photolysis light from interfering with the measurements. In addition, it was necessary to interpose a shutter between the arc lamp and the sample to prevent premature photolysis of the sample by the lamp. When the shutter was opened, a small fraction of the light from the lamp was diverted to a light-activated SCR whose subsequent pulse started the measurement process and fired the photolysis lamp. This kept premature photolysis to a minimum and constant from run to run.

Temperature measurement for the solution work was provided by an iron–constantan thermocouple which was suspended in the center of the cell and whose junction potential was converted directly to degrees Centigrade by a United Systems Corp. Model 465 digital readout thermometer. For gas phase work, the temperature was estimated from a thermocouple taped to the side of the sample cell.

The sample cell was a quartz tube 25 mm in diameter and 23 cm long with a quartz window glued onto each end with epoxy cement. It was wound with nichrome heating wire and could be heated to 100°. For solution work, an auxiliary flask was attached in which the solution was first degassed by the freeze–pump–thaw method and then poured into the cell. The cell was held in a cylindrical aluminum housing which also contained the photolysis lamp. In addition to serving as an explosion shield, the inside of the housing was coated with MgO to reflect the photolysis light.

Materials. 2-Azidobiphenyl was prepared from 2-aminobiphenyl (Aldrich) by the method of Smith and Brown.[2a] The azide was recrystallized from methanol–water to yield light yellow plates, mp 49–50°. The ir spectrum in CCl_4 showed a strong absorption at 2130 cm^{-1}.

Spectrophotometric grade cyclohexane was obtained from J. T. Baker and used as is.

Perfluoroethane was obtained from Du Pont as Freon 116 and used as is.

Phenyl azide was prepared by the method in ref 26 using one-half scale. The azide was distilled at 42° at 3 Torr. Yield was 1.20 g (65%). The ir spectrum showed a strong absorption at 2100 cm^{-1}, indicative of an azide. Kept in a dark bottle at 0°F in a freezer, the azide was stable for *ca.* 6 months.

1-Naphthyl azide was prepared by the method of Smith and Brown[2a] from 1-naphthylamine (Eastman); 5.0 g of amine yielded 4.6 g of azide (78%). Since the azide was too involatile to be distilled, it was purified by elution from a neutral alumina column with CCl_4. The ir spectrum showed a strong absorption at 2110 cm^{-1}.

2-Aminodiphenylmethane was prepared from 2-aminobenzophenone by the method of Hewett, *et al.*;[27] 10.0 g of starting material yielded 7.1 g of product (76%). It was recrystallized from 30–60° petroleum ether yielding hard, white prisms, mp 52–54°.

2-Azidodiphenylmethane was prepared from 2-aminodiphenylmethane by the method of Smith and Brown;[2] 5.0 g of starting material yielded 4.2 g (83%) of product. The azide was purified by distillation at 0.1 Torr using a molecular still and thus no boiling could be measured. The ir spectrum showed a strong absorption at 2140 cm^{-1} and the nmr spectrum in $CDCl_3$ showed a multiplet at δ 6.9–7.2 and a sharp singlet at δ 3.9 with integrated areas in the ratio of 9.2.

Dihydroacridine was prepared from acridine by the method of Bohlmann[28] through a lithium aluminum hydride reduction. The yield was 62%. The product was recrystallized from ethanol yielding white needles melting at 170.5–171.5° The ir spectrum showed a sharp absorption at 3500 cm^{-1} indicating the presence of an N–H bond.

Azepino[2,1-*a*]-11H-indole was prepared by the thermal decomposition of 2-azidodiphenylmethane by the method of Krbechek and Takimoto.[25] The yield was only 21%. It was purified by four recrystallizations from hexane, yielding, finally, white needles, melting at 89–90°.

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(26) "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 710.

(27) C. L. Hewett, L. J. Lermit, H. T. Openshaw, A. R. Todd, A. H. Williams, and F. N. Woodward, *J. Chem. Soc.*, 292 (1948).

(28) F. Bohlmann, *Chem. Ber.*, **85**, 390 (1952).