

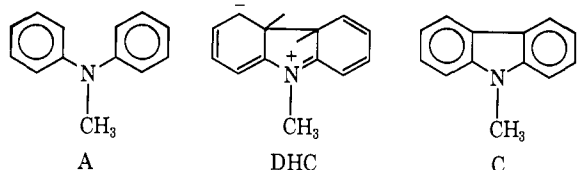
Photoconversion of *N*-Methyldiphenylamine to *N*-Methylcarbazole. Calculated and Observed Quantum Yields as a Function of Oxygen Concentration^{1a}

Gabriela Fischer,^{1b} E. Fischer,^{1b} K. H. Grellmann,^{*1c}
H. Linschitz,^{1d} and Aysel Temizer^{1c}

Contribution from the Max-Planck-Institut für Biophysikalische Chemie, Abteilung Spektroskopie, D-3400 Göttingen, Germany, and the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. Received April 15, 1974

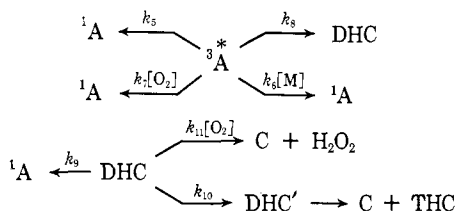
Abstract: The photocyclodehydrogenation of *N*-methyldiphenylamine (A) to *N*-methylcarbazole (C) proceeds via the successive intermediates, ³A and *N*-methyl-4a,4b-dihydrocarbazole (DHC). Oxygen participates in the overall reaction in two ways, by dehydrogenation of DHC to C in competition with its back-reaction to A and by quenching ³A in competition with DHC formation. The quantum yield of carbazole formation as function of [O₂], calculated from this reaction scheme using rate constants determined by flash technique, agrees satisfactorily with experimental values. The effect of light intensity and oxygen concentration on the decay rate of DHC is also reported.

Extended studies of the photoconversion of *N*-methyldiphenylamine (A) to *N*-methylcarbazole (C) have led to the following conclusions.^{2,3} The reaction proceeds exclusively via the amine triplet, ³A, to give an unstable intermediate, characterized by its absorption peak at 610 nm and assigned to the cyclized product, *N*-methyl-4a,4b-dihydrocarbazole (DHC). This is dehydrogenated, either by oxygen or in degassed solution by disproportionation, via the relatively stable *N*-methyl-4,4a-dihydrocarbazole (DHC')⁴ to yield C. In the kinetic scheme corresponding



to these reactions (Scheme I) M represents adventi-

Scheme I



tious quenchers and THC the disproportionation product tetrahydrocarbazole.⁴ This scheme accounts

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(2) (a) H. Linschitz and K. H. Grellmann, *J. Amer. Chem. Soc.*, **86**, 303 (1964); (b) K. H. Grellmann, G. M. Sherman, and H. Linschitz, *ibid.*, **85**, 1881 (1963).

(3) (a) E. W. Förster and K. H. Grellmann, *J. Amer. Chem. Soc.*, **94**, 634 (1972); (b) E. W. Förster and K. H. Grellmann, *Chem. Phys. Lett.*, **14**, 536 (1972); (c) E. W. Förster, K. H. Grellmann, and H. Linschitz, *J. Amer. Chem. Soc.*, **95**, 3108 (1973).

(4) K. H. Grellmann, W. Kühnle, and Th. Wolff, to be submitted for publication.

for the observed maximum in the carbazole quantum yield, Φ'_C , as function of oxygen concentration² (the primed notation, Φ'_C , refers to the quantum yield in the presence of oxygen). At low [O₂], Φ'_C increases with [O₂] because the aerobic conversion of DHC to C (*k*₁₁) competes with the relatively slow back-reaction, *k*₉. At higher [O₂], Φ'_C decreases with [O₂] because oxygen quenching of the triplet (*k*₇) competes with the relatively fast formation of DHC (*k*₈).

In previous work, we have compared the experimentally determined variation of Φ'_C with [O₂] with that calculated from the above scheme, using values of the various rate constants measured independently by flash technique and taking the primary triplet yield as an adjustable parameter.² Semiquantitative agreement was obtained. We now report new measurements of Φ'_C as a function of [O₂] which, together with recent values of the rate constants,^{3c} permit more searching tests of the proposed mechanism (Scheme I). In this connection, we have further studied the "rate constant," *k*₁₁, and show that it depends on light intensity and oxygen concentration.

To establish clearly the shape of the Φ'_C vs. [O₂] function requires measurements over a wide range of oxygen concentration, extending down to very low values. This introduces experimental difficulties caused by the depletion of oxygen in the solution when the reaction is carried far enough to allow accurate product analysis. To overcome this, reactions were run at essentially constant [O₂], by bubbling oxygen-nitrogen mixtures of known composition through the solution during irradiation.⁵

Experimental Section

Materials. The solvent used throughout this work was methylcyclohexane purified by passage through alumina-silica.⁶ The solvent cutoff (50% transmission) was at 220 nm. *N*-Methyldiphenylamine was E.K. analytical grade, used without further purifications.

Procedures. (A) **Nitrogen-Oxygen Mixtures.**⁵ Commercial 10-l. steel bottles were filled with oxygen or air at atmospheric pressure. Tank nitrogen (less than 5 ppm oxygen) was then added to

(5) T. Knittel, G. Fischer, and E. Fischer, *Tetrahedron Lett.*, 2853 (1972).

(6) W. Kühnle, Woelm Information 5a.

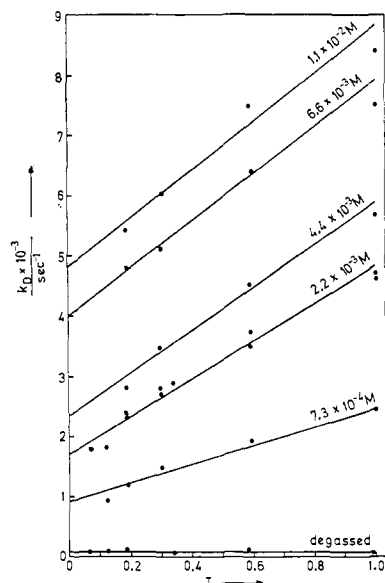


Figure 1. Effective rate constant k_D as function of relative flash excitation intensity I at different oxygen concentrations. The oxygen concentrations in the solutions are indicated for each curve.

various pressures, up to 50 kg/cm². For further oxygen dilution, the process was repeated once or twice, as required. At the highest dilution, providing an oxygen partial pressure of 0.03 Torr over the bubbled solution, the oxygen impurity of the nitrogen (0.004 Torr) was taken into account. The total pressure could be measured with an accuracy of 5%. In all cases, test solutions were first flushed with nitrogen for 20 min at -78° , then with the required gas mixture for 15 min at -78° and for another 10 min at 0° . Cells used in the steady irradiation experiments were provided with a Dry Ice cooled upper section, to trap and reflux evaporated solvent. This prevented any appreciable solvent loss when flushing at rates sufficient to maintain constant $[O_2]$ at room temperature and the lowest oxygen partial pressures.

(B) Irradiations. All measurements were made at room temperature. Steady irradiation experiments utilized 313-nm light isolated from a medium-pressure mercury lamp by an interference filter. Solutions were illuminated in a cell of 10×10 mm cross section, mounted directly in the compartment of a Cary-17 spectrophotometer, and stirred during irradiation by bubbling with the gas mixture. Total irradiation times were several minutes at amine concentrations around $10^{-4} M$. An air-saturated amine solution (o.d. = 0.7 at 313 nm) served as actinometer and was illuminated under the same conditions as the test solution at the beginning of each run. Carbazole formation in the actinometer solution was constant within 5% during the entire set of experiments. Flash experiments were performed in cells of 3 or 10 cm measuring light path, with rectangular cross sections of 4×16 or 3×12 mm, mounted between two flash lamps connected in series.⁸ Calibrated wire mesh screens were inserted between the lamps and cell, to vary the flash intensity. Oxygen concentrations were controlled by flushing with the required gas mixture, as described above. Amine concentrations were in the range $1-2 \times 10^{-4} M$, unless otherwise stated.

(C) Analysis. In the steady illumination experiments, carbazole formation was followed by the characteristic sharp band at 343 nm, using the expanded (0.0–0.1) scale of the Cary-17. The extent of conversion of amine to carbazole never exceeded 15%. In deoxygenated solution, very little carbazole is formed at room temperature, but a side reaction causes an ill-defined increase in absorbance below 380 nm. In the presence of oxygen, this effect persists and is superimposed on the carbazole peak at 343 nm. The height or area of the latter was therefore taken with respect to a corrected base line, corresponding to the absorption without the 343-nm peak. Separate experiments with amine solutions which were first illuminated in the absence of oxygen and then with a known concentration of oxygen showed that this procedure gave the correct carbazole concentration.

Relative quantum yields of carbazole formation were found from the slopes of plots of corrected 343-nm absorption against irradiation time. The linearity of these plots throughout a given run, particularly at low $[O_2]$, gives evidence that the bubbling technique

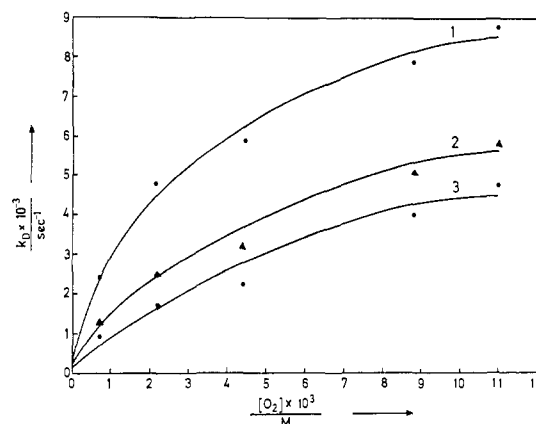


Figure 2. Effective rate constant k_D as function of oxygen concentration at full flash intensity I (curve 1), reduced flash intensity (0.25 I) (curve 2), and extrapolated to zero flash intensity (curve 3).

indeed maintained constant oxygen concentration throughout the irradiation period. The relative quantum yields were converted to absolute Φ'_C values using the actinometric measurement in air-equilibrated solutions.^{3c}

In the flash experiments, DHC transient absorbance at 610 nm was followed as a function of time.^{2,3} In $2 \times 10^{-4} M$ solution, the conversion of A into DHC was about 1% per flash at full intensity.

Results and Discussion

1. DHC Decay. While the detailed mechanism of DHC oxidation by oxygen is not a primary concern in this paper, kinetic complexities in this reaction must be considered in checking Scheme I. Accordingly, the effects of light intensity and oxygen concentration on " k_{11} " have been further studied in the present work.

(A) Dependence on Flash Intensity. Flash photolysis experiments were carried out, varying the flash intensity over about a 20-fold range, as described above. In all cases, the decay of the 610-nm (DHC) flash transient was strictly first order, with a single rate constant throughout a given decay profile, and the initial $[DHC]$ decreased linearly with decreasing flash intensity. Figure 1 shows the effective first-order rate constant, $k_D = 1/\tau$, as function of relative flash intensity, for a series of solutions, equilibrated at various oxygen partial pressures from 1 atm down to 5 Torr. It is seen that the rate constant increases with increasing flash intensity. Also, the effect becomes more marked with increasing oxygen concentration. In nitrogen-bubbled solution, $k_D (=k_9 + k_{10})$ is independent of flash intensity. A slight effect of $[A]$ on the DHC lifetime was also noted. At constant flash intensity and $[O_2] = 2 \times 10^{-3} M$, decreasing $[A]$ from 10^{-4} to $10^{-5} M$ with a corresponding eightfold decrease in initial $[DHC]$ causes about a 25% decrease in k_D .

(B) Dependence on Oxygen Concentration. Figure 2 shows the variation of k_D with oxygen partial pressure in the range 3–750 Torr, at two excitation intensities. In addition, Figure 2 gives limiting values of the first-order rate constant, extrapolated to zero flash intensity.

According to Scheme I the overall rate constant for DHC decay should be $k_D = k_9 + k_{10} + k_{11}[O_2]$. In our flash experiments at the lowest oxygen pressure (5 Torr), $[O_2]$ is about $6 \times 10^{-6} M$ and the initial $[DHC]$ is not greater than about $2 \times 10^{-6} M$. Thus, $[O_2] \gg [DHC]$ throughout, and k_D should vary linearly with $[O_2]$. The results (Figure 2) indicate definitely that this is not the case. The various kinetic effects show that

the mechanism of DHC dehydrogenation by oxygen is a rather complex reaction which merits further investigation.

2. Variation of Φ'_C with $[O_2]$. We have shown³ that in purified, degassed solvents the triplet state of the amine, 3A , decays entirely to DHC, k_5 and $k_6[M]$ are negligible, and therefore $\Phi_{Tr} = \Phi_{DHC}$. The triplet yield is not expected to be appreciably affected by oxygen, because the amine fluorescence yield, Φ'_F , in oxygen saturated solutions is only slightly reduced, relative to that in deaerated solutions ($\Phi_F = 0.04$). The quantum yield of carbazole formation in the presence of oxygen, Φ'_C , is then given by

$$\Phi'_C = \Phi_{Tr} \frac{k_8}{k_8 + k_7[O_2]} \frac{k_{10} + k_{11}[O_2]}{k_9 + k_{10} + k_{11}[O_2]} \quad (1)$$

The triplet quantum yield is evaluated as follows.³ In air-equilibrated solution, DHC is converted quantitatively to carbazole. Since the quantum yield of carbazole in this case is $\Phi'_C = 0.42$, Φ'_{DHC} is also 0.42. Comparative flash experiments in degassed and aerated solution show that $\Phi_{DHC} = 2.0 \times \Phi'_{DHC} = 0.84$, whence Φ_{Tr} is also 0.84. The remaining rate constants, k_7 – k_{11} , are given in Table I, which compares values obtained from flash experiments³ with those adjusted here within experimental error to give the best fit to our Φ'_C measurements. For " k_{11} ," we take the value extrapolated to zero flash intensity (Figure 1, $[O_2] = 2.2 \times 10^{-3} M$) which presumably best corresponds to steady illumination conditions.

Figure 3 shows the dependence of Φ'_C on $[O_2]$ found experimentally and that calculated from eq 1 using $\Phi_{Tr} = 0.84$ and the rate constants of Table I. These results, covering a range in $[O_2]$ of more than four orders of magnitude, considerably extend our previous measurements.^{2,3} From Figure 3 and the comparative values of the two sets of k 's in Table I, we may conclude that Scheme I, corrected for the complications in k_{11} , completely accounts for the reaction kinetics. In particular since the values of k_8 , k_9 , k_{10} , and k_{11} are obtained directly from flash measurements of DHC yields or decay rates, the proposed role of the DHC intermediate, which has been questioned,⁷ is confirmed.

(7) (a) H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 7270 (1970); (b) H. Shizuka, Y. Tajayama, T. Morita, S. Matsumoto, and I. Tanaka, *ibid.*, **93**, 5987 (1971).

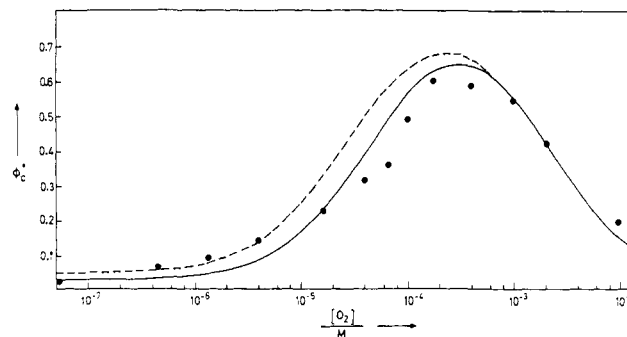


Figure 3. Relative carbazole quantum yield Φ'_C as function of oxygen concentration: solid line, calculated from eq 1 using the rate constants in Table I, column 3; dashed line, Table I, column 2; full circles, measured relative quantum yields, adjusted to the measured absolute value (0.42) at $[O_2] = 2 \times 10^{-3} M$. Oxygen concentrations were calculated from oxygen partial pressures, taking $[O_2] = 1.1 \times 10^{-2} M$ in methylcyclohexane at 750 Torr (I. C. Gjaldbaek, *Acta Chem. Scand.*, **6**, 623 (1952)).

Table I. Rate Constants Derived from Flash Photolysis and Quantum Yield Data at 20°

Rate constant	From flash	From quantum yield
$k_7 (M^{-1} \text{ sec}^{-1})$	$3 \times 10^{10}{}^a$	3×10^{10}
$k_8 (\text{sec}^{-1})$	6.3×10^7	6.3×10^7
$k_9 (\text{sec}^{-1})$	21	35^b
$k_{10} (\text{sec}^{-1})$	1.2	1.2
$k_{11} (M^{-1} \text{ sec}^{-1})$	$8 \times 10^{10}{}^c$	8×10^5

^a From W. Ware, *J. Phys. Chem.*, **66**, 455 (1962). ^b Φ'_C is very sensitive to a change in k_9 . The dashed line in Figure 3 is calculated with $k_9 = 21 \text{ sec}^{-1}$. Due to the high activation energy of the ring opening reaction this variation in k_9 is within experimental error. ^c Value extrapolated to zero flash intensity (Figure 1, $[O_2] = 2.2 \times 10^{-3} M$).

The data of Figure 3 appear to differ substantially from the results of Shizuka, *et al.* (Figure 4 in ref 7b), who report somewhat similar experiments but over a much smaller concentration range. Differences in technique, particularly involving depletion of oxygen at low $[O_2]$, may be responsible for these discrepancies.

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