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INVESTIGATION OF ORGANIC COMPOUNDS FOR THERMAL PROTECTION

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Thermal Protective Materials Research Section
Clothing and Organic Materials Division
U. S. Army Natick Laboratories
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by

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ABSTRACT

The photodissociation study of a purified tetrakis (p-octyl phenyl) hydrazine (TPOPH) in benzene (10^{-4}M) has shown that the recombination rate constant is independent of wavelength in the region of the two major absorption peaks. The recombination follows second-order kinetics for at least 2.5 half-lives. The average initial half-life is 35.4 ± 2.4 msec, excluding the low absorption region at 500-600 mμ. At 560 mμ the decay is first order. It is not clear whether this reaction is associated with TPOPH or with impurity.

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I. INTRODUCTION

This program continues work begun under the title, "Investigation of Organic Compounds for Thermal Protection" (ref. 1). The ultimate objective of the research is development of a photochromic system to provide protection against the electromagnetic radiation pulses from nuclear detonations.

Previous work had shown that solutions of the tetra-aryl hydrazines photodissociate with good reversibility, producing significant absorptions in the visible region of the program.

The design of the kinetic spectroscopy apparatus and a preliminary survey of the photodissociation behavior of several substituted hydrazines are summarized in reference 1. Of the hydrazines studied, the N,N'-tetrakis(p-octylphenyl)hydrazine (TPOPH) in benzene solvent possessed the favorable characteristic of high reversibility. This report describes the results obtained for this system with a purified sample of TPOPH and presents a tentative classification of the nature of the transitions observed in the visible region. These assignments are suggested in order to guide future work in obtaining spectral coverage over the whole visible range.

II. EXPERIMENTAL RESULTS

A. PURITY OF TPOPH

The TPOPH that had been used for the preliminary survey of potentially useful compounds has been subjected to further purification by repetitive recrystallization. The white solid obtained has a narrow melting point range of 139-140°C. The ultraviolet spectrum of this material in ethanol and n-hexane showed only two low-intensity peaks above 250 mμ. This was in agreement with the reported spectrum of its homologue unsubstituted tetraphenyl hydrazine (ref. 2). An attempt was made to purify TPOPH by zone refining, but the hydrazine formed a glass upon solidification.

B. RESULTS OF THE FLASH PHOTOLYSIS OF TPOPH IN BENZENE

The purification of TPOPH proved to be important for both reproducibility and accuracy. Figure 1 is a graph illustrating the variation of the optical density at various wavelengths during the course of the decay of the transient species. The two bands observed peak at 730 mμ and 430 mμ, the former having the larger extinction coefficient. The bands were found to follow second order kinetics for at least two and one-half half lives. The initial half lives are 37.5 ± 2.4 msec and 33.2 ± 2.4 msec for the 730 mμ and 430 mμ bands, respectively, and 35.4 ± 2.4 msec for the combined average*. The half widths of the bands determined on the measured portion of the curve were unaltered during the decay. All experiments were performed at ambient temperature (20 ± 2°C) on a 10^{-4} M sample in benzene with 50-joule flash energy.

Lewis and Lipkin (ref. 3) have conclusively shown that the 730 mμ band is associated with the absorption of the biphenyl amino radical. That the half lives for both bands are identical within the precision of measurement implies that the 430 mμ band also is attributable to the free radical. The solvent filters out all wavelengths below 280 mμ. Since the filtration of wavelengths below 280 mμ removes the high energy region that would lead to photoionization, the absorption band of the ground state of TPOPH peaking at 295 mμ is associated with N-N bond cleavage as the major process. This would explain why we do not see the peaks at 630 mμ (ϕ_2N^+ absorption band) that Lewis observed with a more transparent solvent. Indeed, the high reversibility of TPOPH in benzene compared to cyclohexane and methyl alcohol may be attributable to the suppression of photoionization reactions.

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*Average deviations given.

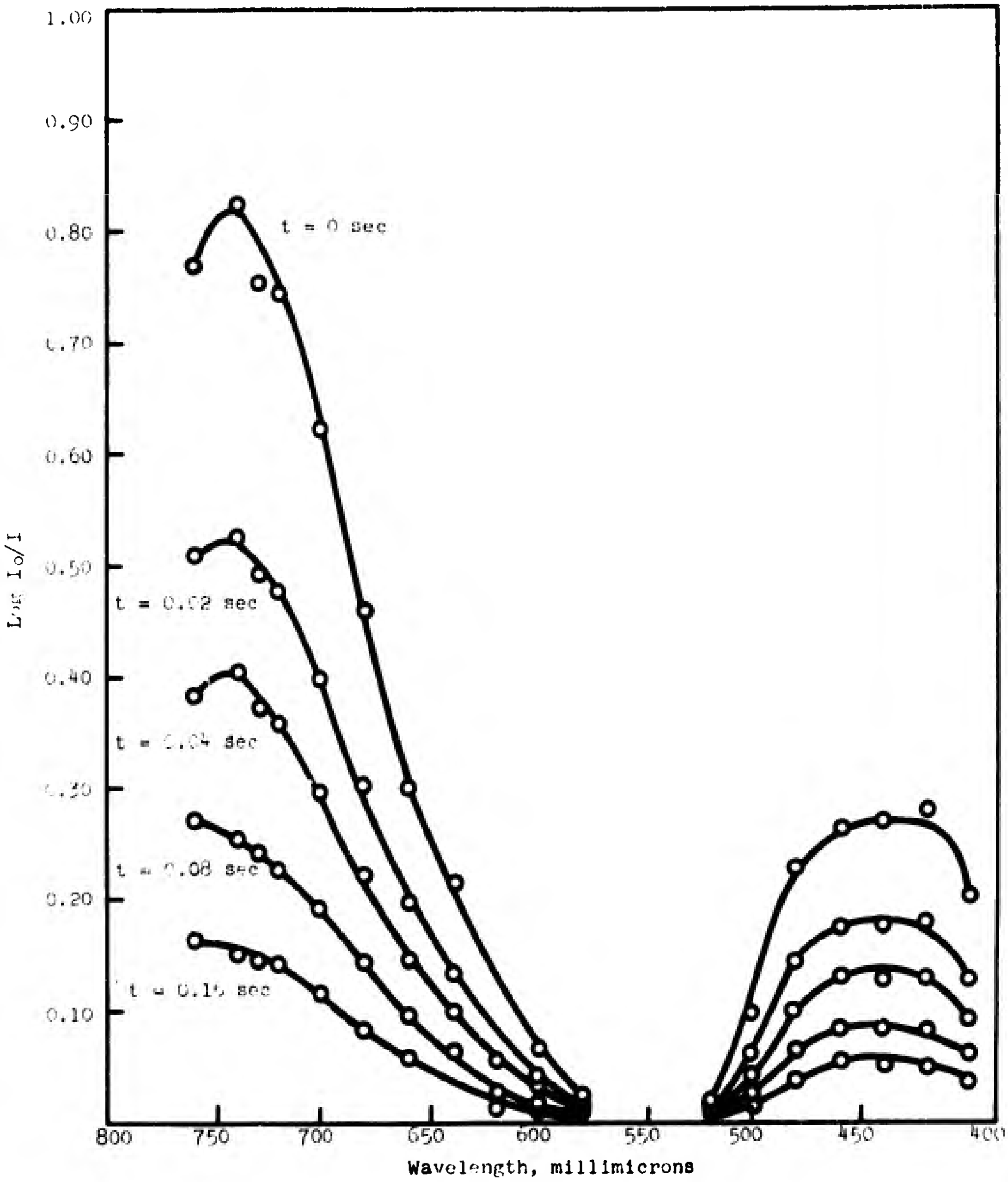


Figure 1. **Decay of absorption of the bis(p-octyl phenyl)amino radical 10^{-4}M TPOPH in benzene at room temperature and 50 joules flash energy.**

The band shape is defined partly by the population distribution of the radicals in vibration and rotational levels. It has been noted earlier that the shapes of the bands are unaltered during the decay. This suggests that the moment that the radicals are detected [i.e., at the end of the excitation (10 μsec)], the radicals have equilibrated with the surroundings. Further, the shape of the curve found at 90°K (ref. 3) for the 730 mμ band is the same to a first approximation, as that we observed at 300°K. On this basis, it can be said that there is only a minor temperature effect on the absorption band and that the radical is in its ground vibrational level. Since Lewis and Lipkin did not investigate the 430 mμ band, no similar conclusions can be drawn for that band. Thus, the interpretation of the rate of recombination is considerably simplified.

On the other hand, no interpretation can be made concerning the degree of thermal excitation since the Doppler broadening of the band is not expected to be large owing to the high mass of the biphenyl amino radical. The extent of the effect of non-equilibrium translational excitation can be studied by varying the wavelength of excitation (which may introduce complicating side reactions) or the temperature coefficient of the recombination rate constant. In the latter case, an Arrhenius plot of the second order rate constant vs temperature should be linear if the biphenyl amino radical is thermalized before it leaves its initial site of formation. Therefore, a careful study of the shape of the absorption band with decay time (assuming no complicating side reactions are involved) and the temperature coefficient reveals the state and degree of excitation of the radicals.

There appears to be a first order process in the region of 500-600 mμ manifesting itself as a deviation from second order kinetics of the observed bands. At 560 mμ the decay is pure first order. Since the optical density is very low, it would be premature at this stage of the investigation to assign this decay to TPOPH or to an impurity.

III. DISCUSSION AND FUTURE WORK

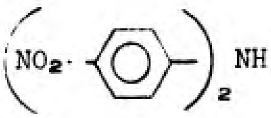
Continuation of the study of the photodissociation of TPOPH in benzene is worthwhile for two reasons. First, the unreactive hydrogens on the aromatic ring improve reversibility. Second, it conveniently permits the study of free radicals alone without the complicating side reactions associated with the production and further reaction of the amino cation. The ionization reactions are inhibited by filtration of wavelengths below 280 mμ by benzene. The possibility that benzene itself may be a sensitizer in this system was ruled out by using benzene itself as a filter solution in the jacket surrounding the reaction vessel. All wavelengths absorbed by benzene were removed before they impinged upon the test solution. No change was observed in the photodissociation reactions, implying that benzene is not a catalyst under the conditions of these experiments.

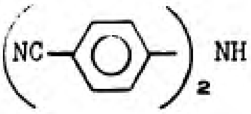
The ultimate objective of investigating any given system is to construct a transient specie that is optically active in the visible spectrum and that has a high extinction coefficient. It is therefore important to determine the wavelength band for a given transition in both the undissociated molecule and its corresponding transition in the free radical. With this knowledge. the search for a suitable combination of solvent on substituted tetraphenyl hydrazine would be placed on a firmer foundation.

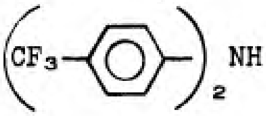
It is helpful at this point to postulate the type of transitions observed in the visible region by the biphenyl amino radical. Tentative assignments will be necessary to determine the area for future work. There are three chromophores in the radical, namely, the aromatic ring, the lone electron pair on the nitrogen atom, and the free electron. In the transitions of the benzene ring itself, there are again three types of excitation, the K, B and R (ref. 4). Each is affected differently by substituents attached to the ring and by polarity of solvent with respect to the direction of the spectral shifts and the variation of the extinction coefficients. The excitation of a lone pair electron is known to be influenced by polar solvents having a labile hydrogen atom. In this type of solvent, a hydrogen bond is formed between the solvent and the lone pair, decreasing the energy of the lone pair electrons without affecting the excited state. These $n \rightarrow \pi$ transitions are known to have spectral shifts to lower wavelengths by 30 mμ or more. The electron spin resonance studies of the biphenyl amino radical have shown that the free electron's charge density is not measurably influenced by a hydrogen donating solvent. Therefore, a further seies of experiments in alcohol, at low temperature to reduce abstraction reactions, would be very valuable in location of the $n \rightarrow \pi$ transition.

Following is a tentative list of secondary amines to be considered for preparation and subsequent dimerization to their hydrazine derivatives:

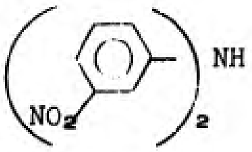
Electron withdrawing groups

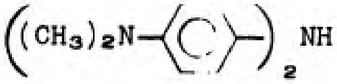


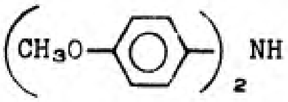


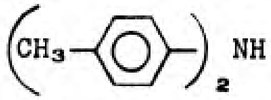


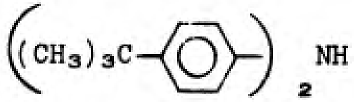
Electron donating groups

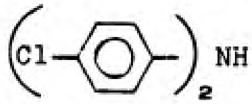












The proposed solvents are benzene, acetonitrile, n-hexane, and ethanol.

We plan to conduct experiments on the absorption spectrum of tetraphenyl hydrazine and its derivatives in various solvents. The flash photolysis of the compounds will be performed on the most promising systems.

Finally, the extent of the spectral shift of ϕ_2N will be strongly influenced by the configuration it attains while unassociated. The ground configuration is most probably nearly planar, with the lone pair electrons in resonance with the unoccupied π bond of the phenyl ring. Upon dissocation, the radical will have a strong tendency to form a linear configuration,

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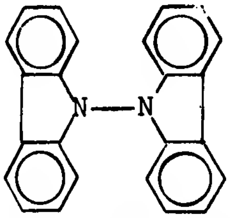
This configuration lowers the energy of the lone pair and the frequency of excitation shifts to the red, i.e., toward the visible. It will be of interest to photodissociate the sterically hindered hydrazine,



to determine the direction and magnitude of the spectral shift of the free radical of this hydrazine where linearization is frustrated.

IV. CONCLUSIONS AND SUMMARY

Photodissociation studies of purified TPOPH in benzene have shown that the recombination rate constant is independent of wavelength (with the possible exception of the 500-600 mμ window. The recombination follows second-order kinetics for at least 2.5 half-lives. At 10^{-4}M the average initial half life (excluding the low absorption 500-600 mμ region) is 35.4 ± 2.4 msec.

The decay of the small absorption at 560 mμ has been found to be first order. It is not yet clear whether this reaction is associated with TPOPH or impurity.

Relatively straightforward experiments are outlined to confirm tentative transition assignments as an aid in determination of substituents and solvents to meet the program requirements of high absorption coefficients throughout the visible spectrum.

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