Photoreduction of Aromatic Nitro Compounds by Tri-*n*-butylstannane

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Abstract: Photochemical reductions at 366 mμ of nitrobenzene and 1-nitronaphthalene in benzene solutions containing tri-*n*-butylstannane have been studied. The hydrogen abstraction rate constants for these molecules were determined to be 4×10^8 and $<3 \times 10^6$ M^{-1} sec^{-1}, respectively. Hydrogen atom abstraction by 1-nitronaphthalene results in 1-naphthylamine which was identified by its fluorescence spectrum. The photochemistry of 1-nitronaphthalene in stannane is similar to that reported by other workers for 1-naphthaldehyde. The ratio of hydrogen atom abstraction rate constants in tri-*n*-butylstannane relative to isopropyl alcohol is greater for $(\pi,\pi^*)^3$ than for $(n,\pi^*)^3$.

Previous photochemical studies from this laboratory have shown that nitrobenzene undergoes hydrogen abstraction in isopropyl alcohol which proceeds *via* the n,π^* triplet.[1] The lack of photochemical hydrogen abstraction by 1-nitronaphthalene in isopropyl alcohol coupled with its long-lived phosphorescence at 77°K provided evidence for a low-lying π,π^* triplet. In view of the relatively long-lived triplet of 1-nitronaphthalene in solution, $k_{dt} < 4 \times 10^5$ sec^{-1}, it would appear that the availability of an efficient hydrogen donor such as tri-*n*-butylstannane may result in photoreduction in the same manner as has been observed with 1-naphthaldehyde and 2-acetonaphthone.[2-4] Furthermore, the rapid deactivation of the nitrobenzene triplet ($\sim 10^{-9}$ sec) should provide information as to whether or not the hydrogen abstraction rate constant, k_H, is significantly different in tri-*n*-butylstannane relative to isopropyl alcohol. Recent investigations from other laboratories[2-4] have shown that k_H in tri-*n*-butylstannane for ketones possessing low-lying π,π^* triplets lie in the range 0.5–1.3 $\times 10^6$ M^{-1} sec^{-1}, which is the same value measured for benzophenone in isopropyl alcohol.[5] If the stannane reduction of nitrobenzene is not faster than isopropyl alcohol, the quantum yield results should be the same for equal concentrations of each hydrogen donor, since rapid deactivation of the nitrobenzene triplet predominates. In the present investigation quantum yield measurements were made on nitrobenzene and 1-nitronaphthalene in benzene solutions containing tri-*n*-butylstannane.

Experimental Section

Chemicals. Zone-refined nitrobenzene (Hinton, Fla.) was used as received. Reagent grade 1-nitronaphthalene was recrystallized twice from hexane. 1-Naphthylamine obtained from Aldrich Chemical Co. was recrystallized from an water–alcohol mixture. Tri-*n*-butylstannane obtained from Alfa Inorganics, Beverly, Mass., was vacuum distilled and stored in vacuum-sealed tubes until ready for use. Spectrograde benzene was used as received.

Apparatus. All photochemical experiments were performed with 366-mμ light using equipment described previously.[1] All samples were degassed by three freeze–pump–thaw cycles at $<10^{-3}$ mm. Fluorescence measurements on 1-naphthylamine obtained as a photoproduct from 1-nitronaphthalene agreed with those of an authentic recrystallized sample. An Aminco monochromator and 1P21 photomultiplier were used for these measurements. Analysis of photolyzed solutions was made with the use of ultraviolet absorption and polarographic analysis.

Results

The quantum yield results for the disappearance of nitrobenzene in benzene solutions containing tri-*n*-butylstannane are presented in Figure 1. The steady-state approximation for this system is given by the expression[2]

$$\frac{1}{\Phi} = \frac{1}{\phi_T} + \frac{k_{dt}}{\phi_T k_H(\mathrm{Bu_3SnH})}$$

where Φ is the disappearance quantum yield of nitrobenzene arising from hydrogen abstraction, ϕ_T is the triplet yield of the photoexcited molecule, k_{dt} and k_H are rate constants for deactivation of the triplet and hydrogen abstraction, respectively, and (Bu_3SnH) is the concentration of tri-*n*-butylstannane. The concentration of nitrobenzene was 2.0×10^{-2} M and the intensity of light at 366 mμ was determined to be 1.3×10^{16} quanta/sec. Evidence for the hydrogen abstraction was the appearance of azoxybenzene in the ultraviolet spectra. Azoxybenzene results from a coupling reaction following oxidation of phenylhydroxylamine to nitrosobenzene which was observed in isopropyl alcohol solutions.[1] The slope of the data in Figure 1 is 3.4 M^{-1}, and since the intercept gives the triplet yield which has been determined by energy transfer studies to be 0.67,[1] it follows that $k_{dt}/k_H = 2.28$ M^{-1}. The rapid deactivation of the nitrobenzene triplet ($\sim 10^9$ sec^{-1}) has been reported previously; consequently, the hydrogen abstraction rate constant for the nitrobenzene triplet in tri-*n*-butylstannane is 4×10^8 M^{-1} sec^{-1}. This rate constant is significantly larger than the value reported for the hydrogen abstraction process in stannane for such ketones as 1-naphthaldehyde and 2-acetonaphthone.[2-4] This result is evidence for an efficient n,π^* hydrogen abstraction by nitrobenzene, which results in a low disappearance quantum yield in isopropyl alcohol due to rapid deactivation of the triplet.

The quantum yield for the disappearance of nitrobenzene in 2.02 M tri-*n*-butylstannane was determined to be 0.25 ± 0.01, which is a considerable increase

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(1) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966); **89**, 6917 (1967); **90**, 1949 (1968).

(2) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

(3) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

(4) J. Osugi, S. Kusuhara, and S. Hirayama, *Rev. Phys. Chem. Jap.*, **36**, 93 (1967).

(5) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

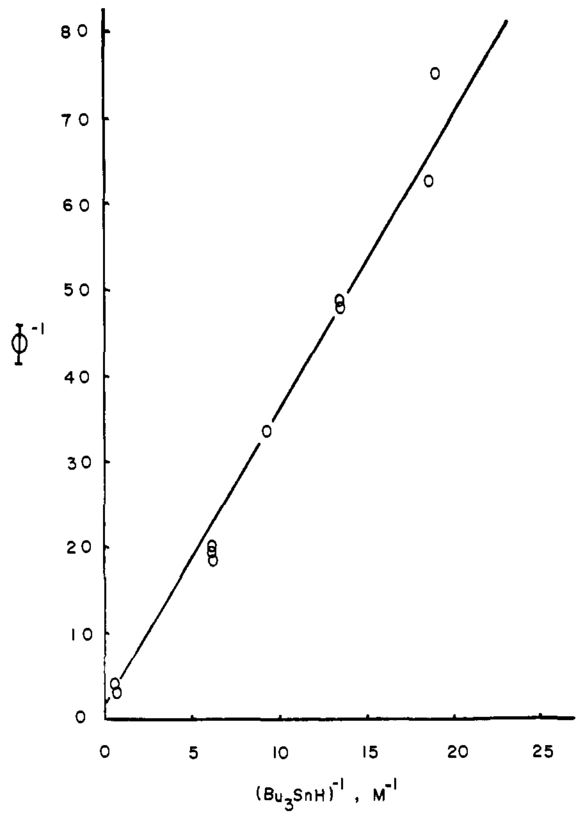


Figure 1. Inverse photochemical disappearance quantum yields at 366 mμ for 2.0×10^{-2} M nitrobenzene in benzene solutions containing tri-*n*-butylstannane as hydrogen donor. Degassed solutions at 25°.

over the value of 1.14×10^{-2} for nitrobenzene in pure isopropyl alcohol (13 M).

The results for 1-nitronaphthalene in benzene solutions containing stannane appear to be analogous to those observed with 1-naphthaldehyde. Evidence for the hydrogen abstraction process was obtained by the appearance of 1-naphthylamine which fluoresces in benzene with a wavelength maximum of 390 mμ. We were unable to find any evidence of an intermediate photoproduct preceding the formation of 1-naphthylamine. A referee has suggested the possibility that the first hydrogen abstraction in 1-nitronaphthalene may involve the ring hydrogen; however, the lack of photoreduction for this molecule in isopropyl alcohol indicates that the ring hydrogens are not involved. Further identification by comparison with an authentic sample was made by measuring the absorption and fluorescence spectra of the hydrochloride which shifts to shorter wavelengths upon protonation of the amine. The concentration of 1-nitronaphthalene was generally 7.7×10^{-4} M and intensities were typically 1.2×10^{16} quanta/sec. The results presented in Figure 2 indicate a slope of 0.25 M^{-1}, which together with the triplet yield of 0.63 and $k_{dt} < 4 \times 10^5$ sec^{-1}, determined elsewhere,[1] indicate the hydrogen abstraction rate constant to be $<3 \times 10^6$ M^{-1} sec^{-1}.

Table I. Photochemical Hydrogen Atom Abstraction Rate Constants in Isopropyl Alcohol and Tri-*n*-butylstannane

	Isopropyl alcohol k_H, M^{-1} sec^{-1}	Tri-*n*-butylstannane k_H, M^{-1} sec^{-1}
Benzophenone[a]	1.28×10^6	
Acetone[b]		8×10^8
1-Naphthaldehyde[c]		5.5×10^5
2-Acetonaphthone[c, d]		9.0×10^5, 1.3×10^6
Nitrobenzene[e]	0.8×10^6	4×10^8
1-Nitronaphthalene[e]	$<10^2$	$<3 \times 10^6$

[a] Reference 5. [b] Reference 6. [c] Reference 2. [d] Reference 4. [e] This work and ref 1.

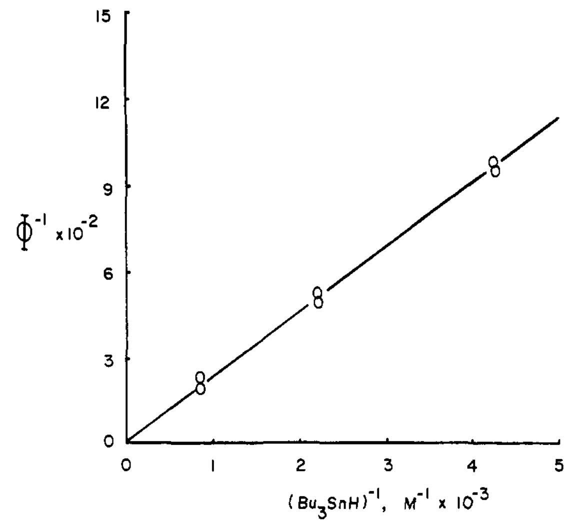


Figure 2. Inverse photochemical disappearance quantum yields at 366 mμ for 7.7×10^{-4} M 1-nitronaphthalene in benzene solutions containing tri-*n*-butylstannane as hydrogen donor. Degassed solutions at 25°.

A summary of the rate constants determined in this work and those reported by other laboratories for carbonyl compounds is presented in Table I.

Discussion

It is evident that the nitrobenzene triplet undergoes hydrogen abstraction in tri-*n*-butylstannane and isopropyl alcohol, whereas 1-nitronaphthalene is photochemically active only in the former. The results for nitrobenzene in stannane indicate an unusually rapid hydrogen abstraction rate constant which is $>10^2$ larger than the values reported for aromatic ketones containing π,π^* triplets. The large rate constant between nitrobenzene and stannane agrees with recent work on the photoreduction of acetone in stannane.[6] The hydrogen abstraction rate constant for the n,π^* triplet was reported to be 8×10^8 M^{-1} sec^{-1}.

The results for 1-nitronaphthalene confirm the assignment of the low-lying π,π^* triplet as the cause of inefficient hydrogen abstraction in isopropyl alcohol.

Recently, Barltrop and Bunce[7] concluded that the lowest triplet of nitrobenzene is π,π^* on the basis of long-lived emission at 77°K. From our results presented here and elsewhere,[1] we believe that their assignment is incorrect. Experiments repeated many times in our laboratory with vacuum-distilled and zone-refined nitrobenzene have shown that the nitrobenzene triplet does not give long-lived emission and that the phosphorescence yield is $\leq 10^{-3}$. Furthermore, correspondence from Professor P. de Mayo[8] confirms

(6) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2504 (1967).

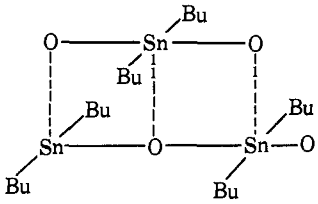
(7) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc., C*, 1467 (1968).

(8) We are very grateful to Professor P. de Mayo from the University of Western Ontario, for informing us of his results regarding the lowest triplet of nitrobenzene.

our observations regarding the n,π^* triplet assignment for nitrobenzene and the very weak phosphorescence from purified nitrobenzene. He has noted a strong emission from normal nitrobenzene which disappears to the limit of detection upon purification. It appears, therefore, that the emission reported by Barltrop and Bunce is not that of nitrobenzene, but rather an impurity.

It would appear that the rapid hydrogen abstraction rate constant between nitrobenzene and stannane can be used to good advantage in cases where the hydrogen atom abstraction yield is low as a result of rapid relaxation of the triplet. In fact, it follows from the similarity of the hydrogen abstraction rate constants for the n,π^* triplet of carbonyl and aromatic nitro compounds that n,π^* triplets with lifetimes of 10^{-10} sec, which will not photoreduce in isopropyl alcohol, would have a disappearance quantum yield of ~0.1 in 2 *M* tri-*n*-butylstannane. Thus tri-*n*-butylstannane besides being an efficient hydrogen donor is a useful reagent to provide hydrogen atoms for short-lived n,π^* triplets which relax rapidly relative to the hydrogen abstraction process in isopropyl alcohol.

Previous studies of photoreductions with tri-*n*-butylstannane have tacitly assumed that hydrogen abstraction results in hexabutylditin, which is a liquid.[2,4] Although we observed the disappearance of the Sn–H band at 1820 cm^{-1}, large-scale photolysis of nitrobenzene in benzene solutions of tri-*n*-butylstannane with a 450-W Hanovia mercury lamp and Pyrex filter resulted in precipitation of an amorphous powder, insoluble in organic solvents, which was analyzed to contain oxygen.[9] This substance was identified as polydibutyltin oxide, $[(n\text{-}C_4H_9)_2SnO]_n$, by comparison with the 2–16 μ infrared spectrum reported by Reichle.[10] In addition the far-infrared spectrum of the powder indicated an absorption at 570 cm^{-1} which has been assigned to the asymmetric Sn–O–Sn stretch.[11,12] The presence of a broad band at 400 cm^{-1} has been attributed to the weak bonds between the oxygen atoms of one polymeric chain with the tin atoms of another chain,[12] *i.e.*



It is difficult to account for the formation of polydibutyltin oxide; however, we cannot exclude the possibility that hexabutylditin is formed and then oxidized in a further reaction. The oxidation of hexaethylditin by oxygen has been reported.[13]

From the steady-state expression for the quantum yields in isopropyl alcohol and stannane the following expression relating the ratio of yields in the two solvents can be obtained

$$\frac{\Phi_{\mathrm{IPA}}}{\Phi_{\mathrm{SnH}}} = \frac{k_{\mathrm{H}}(\mathrm{IPA})}{k_{\mathrm{H}}'(\mathrm{Bu_3SnH})}[4.50(\mathrm{Bu_3SnH}) + 1]$$

where k_H and k_H' are the hydrogen abstraction rate constants of interest. The ratio k_H'/k_H may be defined as an enhancement factor for hydrogen abstraction in stannane relative to isopropyl alcohol. Using our previously reported results for nitrobenzene in isopropyl alcohol and those for stannane reported here, the ratio $k_H'/k_H = 530$ for the n,π^* triplet of nitrobenzene. Since 1-nitronaphthalene does not photoreduce in isopropyl alcohol, a lower quantum yield limit of $<10^{-4}$ was used to estimate that $k_H'/k_H > 5.4 \times 10^5$. It would appear that the enhancement factor is greater for π,π^* triplets than for n,π^* triplets. This difference may indicate that the hydrogen abstraction process is different for the two molecules studied.

Acknowledgment. We wish to thank Professor H. Horan for providing us with the far-infrared measurements.

[9] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., analysis: 39.7% C, 7.0% H, 45.3% Sn, and 8.4% O. These values predict two butyl groups per tin atom and 1.3 oxygen atoms per tin atom.

[10] W. T. Reichle, *J. Polym. Sci.*, **49**, 521 (1961).

[11] R. A. Cummins, *Aust. J. Chem.*, **18**, 19 (1965).

[12] D. H. Lohmann, *J. Organometal. Chem.*, **4**, 382 (1965).

[13] Yu. A. Aleksandrov, T. G. Brilkina, and V. A. Shushunov, *Tr. po Khim. i Khim. Tekhnol.*, **4**, 3 (1961); *Chem. Abstr.*, **56**, 492*d* (1962).