Nitrogen Photochemistry. A Time Dependent Photooxidation of Alcohols by Aromatic Nitro Compounds

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The photoreduction of nitrobenzene by alcohols,[2–8] amines,[9] hydrocarbons,[10] and ethers[9] has been documented, and the absorption band of nitrobenzene in the 330-nm region assigned to an n,π^* transition,[11,12] and the hydrogen abstraction process to a triplet of nitrobenzene.[3,14] Hurley and Testa[3] have shown the reduction of nitrobenzene to be quite inefficient at long irradiation times, i.e., the quantum yield for the disappearance of nitrobenzene in 2-propanol is 0.011. The hydrogen abstraction results in the formation of acetone, and the quantum yield of acetone generation is approximately twice that for the disappearance of nitrobenzene.[3,13]

Experimental Section

Chemicals and Equipment. 2-Propanol was purified by distillation from magnesium, 1-propanol was refluxed over $NaBH_4$ and redistilled from magnesium, and nitrobenzene and propanol were distilled immediately before making up samples. 1,3,5-Trinitrobenzene was recrystallized from diethyl ether.

Irradiation of 1,3,5-Trinitrobenzene in 1-Propanol for Isolation of Acetal. A solution containing 1.32 g of 1,3,5-trinitrobenzene in 250 mL of 1-propanol (0.025 M) was prepared and degassed at 5×10^{-4} Torr. The sample was irradiated for 12 h using 366-nm lamps in a Rayonet photochemical reactor. Approximately 200 mL of 1-propanol was removed from the sample by distillation and the acetal collected by GLC on a Wilkens Aerograph Autoprep Model A-700 equipped a 10 × 0.25 in. 20% Carbowax 20M on Chromosorb W column: NMR (CCl_4) δ 1.0–1.6 (m, 15 H) 3.75 (m, 4 H), 4.8 (t, 1 H).

Quantum Yields. The quantum yields were run in a modified Rayonet merry-go-round[14] using a Hanovia 450-W medium-pressure mercury arc lamp. The 366-nm lines were isolated with Corning 0-52-7-37 filter. The samples were degassed four times to 5×10^{-4} Torr in 13 × 100 mm Pyrex tubes, sealed, and irradiated. A modified potassium ferrioxalate actinometry procedure was used.[15] The light intensity was measured before and after the samples were irradiated. After irradiation, the samples were opened and an aliquot was added to a known solution of chlorobenzene as an internal standard. The samples were then analyzed on a Beckman GC-5 using a 20-ft Carbowax on Chromosorb W column at 85 °C (aldehyde and acetal) and 95 °C (acetone). The amountsnofieldehyde and acetal in the dark reaction solution were subtracted from the amounts found in the irradiated samples before the quantum yields were calculated.

Results

The quantum yields of product formation for the 1-propanol–trinitrobenzene, 2-propanol–nitrobenzene, and 1-propanol–nitrobenzene solutions were found to decrease with increasing amounts of radiation, cf. Table I. These quantum yields are based on the amount of carbonyl compound produced both in the free as well as the acetal/ketal form. Only a negligible amount of 2,3-dimethyl-2,3-butanediol was found at the longest irradiation time of the 2-propanol reaction solution. At long irradiation times, the results herein reported are comparable to those reported by Hurley and Testa.[3] That is, at 4.8×10^{-4} einsteins, the quantum yield of acetone formation is 0.022 (this work); and, at 5×10^{-4} einsteins, the quantum yield of nitrobenzene disappearance was reported to be 0.011.

To determine the effect of acid on the irradiation of nitrobenzene in 2-propanol, a reference irradiation in 50% aqueous 2-propanol was compared to that of an acidic 2-propanol solution of nitrobenzene. In the acid solution, the quantum yields did not change (0.080 ± 0.003) with the amount of exposure, contrary to all of the neutral solution results.

The unirradiated portion of each sample was analyzed simultaneously with the irradiated sample and any observed product from a dark reaction compensated for; the optical density of the nitroaromatic solutions were always greater than 2 and the conversion of nitroaromatics was small. The quantum yields reduced in size much faster than sample conversion.

Discussion

The quantum yield change phenomenon observed in these solutions occurs in all four neutral alcoholic and aqueous slutions examined, on two different alcohols and with two different nitroaromatics. The phenomenon does not occur in acid solution. There are two possible explanations for these observations. Impurities could be causing the change or a

Table I. Quantum Yields for the Production of Aldehydes or Ketones

Nitroaromatic (concn), alcohol	Total einsteins × 10^6	Φ
Trinitrobenzene[a] (0.026 M), 1-propanol	12.7	0.071
Trinitrobenzene[a] (0.026 M), 1propanol	25.4	0.041
Trinitrobenzene[a] (0.026 M), 1-propanol	76.2	0.022
Trinitrobenzene[a] (0.026 M), 1-propanol	177.8	0.015
Nitrobenzene (0.098 or 0.195 M), 2-propanol	15.6	0.27
Nitrobenzene (0.098 or 0.195 M), 2-propanol	29.0	0.20
Nitrobenzene (0.098 or 0.195 M), 2-propanol	88.6	0.088
Nitrobenzene (0.098 or 0.195 M), 2-propanol	192	0.052
Nitrobenzene (0.098 or 0.195 M), 2-propanol	338	0.037
Nitrobenzene (0.098 or 0.195 M), 2-propanol	860	0.026
Nitrobenzene (0.098 or 0.195 M), 2-propanol	1030	0.022
Nitrobenzene (0.098 or 0.195 M), 1-propanol	10.9	0.067
Nitrobenzene (0.098 or 0.195 M), 1-propanol	29.5	0.045
Nitrobenzene (0.098 or 0.195 M), 1-propanol	91.0	0.025
Nitrobenzene (0.098 or 0.195 M), 1-propanol	266.0	0.015
Nitrobenzene (0.098 or 0.195 M), 1-propanol	1010.0	0.010
Nitrobenzene (0.0098 M), 2-propanol–water	19.9	0.12
Nitrobenzene (0.0098 M), 2-propanol–water	87.0	0.036
Nitrobenzene (0.0098 M), 2-propanol–water	386.0	0.017
Nitrobenzene (0.0098 M), 2-propanol–12 M HCl	17.9	0.083
Nitrobenzene (0.0098 M), 2-propanol–12 M HCl	114.0	0.079
Nitrobenzene (0.0098 M), 2-propanol–12 M HCl	470.0	0.082

quencher(s) could be formed in the solution as a consequence of the initial photochemical process.

Although it is difficult to rigorously exclude all impurities from the system, impurities probably are not responsible for the observed results because a solvent impurity would not show a dependence on the amount of light absorbed; nitrobenzene and solvents purchased from several sources gave duplicate results, and these results agree with Hurley and Testa's published results at long irradiation times.[3] Thus, the quencher idea is most plausible.

If a quencher is being generated which is not photochemically active, its concentration should be proportional to the total amount of light, and plots of I^0/I vs. E should be linear. Actually, these plots are reasonably linear in the initial stages of the reaction but progressively decrease to zero slope. Thus, the newly formed quencher is also decomposed by light, and its concentration becomes constant after a period of time. Nitrobenzene, itself, is not a quencher since the quantum yields are not dependent on the initial nitrobenzene concentration.

A nitroxide radical(s) is a good candidate for the quencher formed since these are known to be formed under the reaction conditions[13,16,17] and di-*tert*-butyl nitroxide has been used as a triplet quencher.[18] Since nitroxides are destroyed by acid,[16] the 2-propanol–nitrobenzene irradiation was done in an aqueous, acidic solution and the results compared to those from the corresponding neutral, aqueous solution. In acid, the quantum yield remains constant with time, albeit at a lesser value than the initial quantum yield in neutral solution.

The quantum yield effect described herein means that nitrobenzene is more efficient at product formation than earlier recognized. Consequently it is necessary to reevaluate the conclusion of Hurley and Testa[3] that the low quantum yield of nitrobenzene disappearance is due to a short lifetime of triplet nitrobenzene, ca. 10^{-9} s. Their determination was done with the assumption that no complexes are formed between any of the species present. However, nitrobenzene is known to form charge transfer complxes with benzene[19] and piperylene[20] and, furthermore, the formation of such complexes can increase the rates of radiationless processes.

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Registry No.—1,3,5-Trinitrobenzene, 99-35-4; nitrobenzene, 98-95-3; 1-propanol, 71-23-8; 2-propanol, 67-63-0; propanol, 123-38-6; acetone, 67-64-1.

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Ylide Autoxidation during the Stevens Rearrangement

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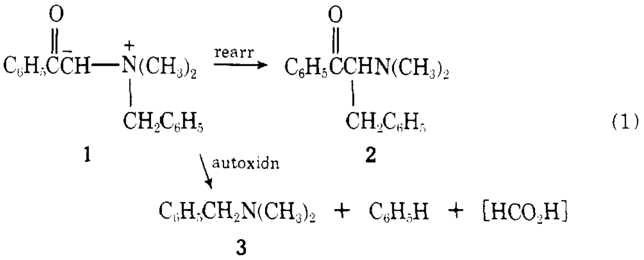
The autoxidation of enolate anions has been studied in detail by Doering and Haines[1] and more recently reinvestigated by Sawaki and Ogata.[2] Although the mechanistic question of a 1,2-dioxetane or an α-keto hydroperoxide intermediate remains unresolved, the overall process of oxidation followed by cleavage is well established.

Carbonyl stabilized ylides provide an example of a special enolate anion in which the onium atom can also participate in the anion stabilization process. Because of our interest in ylide rearrangements[4] it was of concern to know if a similar autoxidation process might occur with these anions. In the following we report our observations that such autoxidation of an ylide does occur competitive with the Stevens rearrangement process at lower temperatures and in those cases when oxygen is present.

Results and Discussion

Ylide **1** smoothly rearranges in chloroform to **2** with a specific rate constant of 5.9×10^{-4} min^{-1} at 0 °C as determined by following the reaction by NMR. The spectral data along with subsequent workup of the reaction mixture showed that dimethylbenzylamine (**3**) was also formed. The ratio of Stevens rearrangement product (**2**) to dimethylbenzylamine (**3**) varied markedly, dependent upon the amount of oxygen present in the reaction mixture (Table I). In addition, the major nonbasic product recovered was benzoic acid in a molar amount similar to the dimethylbenzylamine.



$$\underset{\mathbf{1}}{C_6H_5\overset{O}{\overset{\|}{C}}\overset{-}{C}H\!-\!\overset{+}{N}(CH_3)_2 \atop \quad\quad | \atop \quad\quad CH_2C_6H_5} \xrightarrow{\text{rearr}} \underset{\mathbf{2}}{C_6H_5\overset{O}{\overset{\|}{C}}CHN(CH_3)_2 \atop \quad | \atop \quad CH_2C_6H_5} \qquad (1)$$

$$\mathbf{1} \xrightarrow{\text{autoxidn}} \underset{\mathbf{3}}{C_6H_5CH_2N(CH_3)_2} + C_6H_5H + [HCO_2H]$$

The presence of both dimethylbenzylamine and benzoic acid was of particular interest because of their relationship

Table I. The Effect of Oxygen on Product Distribution[a]

	Rel % products	
Atmosphere	Rearr (2)	Autoxidn (3)
Vacuum[b]	100	0
N_2[c]	76	24
Air[c]	65	35
O_2[c]	37	63
O_2[d]	22	78

[a] Ylide in $CDCl_3$ (0.25 M) at 0 °C. [b] Evacuated and freeze–thaw degassed. [c] Atmosphere over reaction solution. [d] Sample stirred in oxygen atmosphere.