Hydrochloric Acid Catalyzed Photoreduction of Nitrobenzene by 2-Propanol. The Question of Protonation in the Excited State[1a]

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Abstract: Nitrobenzene reacts photochemically in 50% 2-propanol–water containing 6 *M* HCl to give acetone and 2,4-dichloroaniline as the major products. Nitrosobenzene is implicated as a reaction intermediate since it is converted to the observed photoproducts when placed in the reaction medium in the dark. In agreement with an earlier report, addition of HCl (>3 *M*) causes a marked enhancement of quantum efficiency of nitrobenzene photoreduction in 50% 2-propanol–water. When sulfuric acid is substituted for HCl, catalysis of photoreduction does not occur. Using mixtures of HCl and LiCl to maintain [Cl^-] at 6 *M* and vary [H^+], the quantum yield of nitrobenzene loss is found to be constant ($\Phi = 0.15$) in the range 0.05–6 *M* [H^+]. These findings cannot be rationalized by the excited state protonation mechanism suggested by Hurley and Testa and suggest that Cl^- plays an essential role in the HCl catalysis. A mechanism involving electron transfer from Cl^- to photoexcited nitrobenzene as the primary process is presented.

Nitrobenzene undergoes inefficient photoreduction ($\Phi = 0.011$) in 2-propanol to give phenylhydroxylamine and acetone.[2] Nitrobenzene is converted to chloroanilines by irradiation in concentrated aqueous HCl.[3] Following these reports, Hurley and Testa[4] investigated the effect of HCl on the efficiency of nitrobenzene photoreduction. They found that addition of HCl (6 *M*) to 50% 2-propanol–water caused a 36-fold increase in quantum yield of nitrobenzene disappearance. The enhancement of efficiency was attributed to protonation of n,π^* triplet nitrobenzene leading to a more reactive or longer lived oxidant. Protonation followed by hydrogen abstraction from 2-propanol leading to photoreduction products was assumed to compete with a second reaction initiated by chloride ion attack on the aromatic ring.

We were struck by a problem of this proposal, namely, that n,π^* triplet nitrobenzene would be expected to be an extremely weak base. The pK_a of ground state $PhNO_2H^+$ is -11.3[5] and the H_0 of 6 *M* aqueous HCl is -2.12.[6] Ignoring solvent effects, the fraction of ground state nitrobenzene molecules protonated in 50% aqueous 2-propanol containing 6 *M* HCl would be about 10^{-9}. Excitation to an n,π^* triplet state would have the effect of reducing electron density on the nitro oxygens which would be base weakening. Since the n,π^* triplet is also reported to be short-lived ($\tau \sim 10^{-9}$ sec),[7] we felt that efficient protonation would be unlikely. We have therefore undertaken further study of the HCl-catalyzed photoreduction of nitrobenzene designed to test the hypothesis of protonation of nitrobenzene in the excited state.

Experimental Section

Materials. Nitrobenzene (Eastman) was distilled through glass helices (bp 209–209.5°). Gas chromatography showed no detectable impurities. The following materials were used as received: HCl (Matheson Coleman and Bell, reagent), H_2SO_4 (95–97%, Du Pont), LiCl (Fisher), 2-propanol (Matheson Coleman and Bell, Spectrograde), valerophenone (Eastman), benzene (Baker Spectrograde), K_2CrO_4 (Baker reagent), and *n*-dodecane (Matheson). Nitrosobenzene[8] was recrystallized from *tert*-butyl alcohol–water and showed no detectable impurities on gas chromatography.

Instrumentation. Gas chromatography was carried out on a Hewlett–Packard 5750 instrument using either a 0.125 in. × 6 ft SE-30 or a 0.125 in. × 10 ft SE-52 silicone gum rubber column. Uv absorption measurements were made on a Beckman DB-G or a Beckman DU spectrophotometer. Nmr spectra were recorded using a Varian A-60 spectrometer. Preparative irradiations were conducted using a 450-W Hg lamp (Hanovia Model 679A) with a quartz immersion well and a Pyrex 7740 glass filter sleeve. Reaction solutions were stirred magnetically during irradiation and flushed with nitrogen (99.998%) before and during irradiation.

Quantum Yields. Quantum yields were determined using a merry-go-round (MGR-500, Southern New England Ultraviolet Co.), 450-W Hanovia lamp, and Pyrex 16 × 150 mm test tubes. Tubes containing 10-ml samples of nitrobenzene (2.0×10^{-3} *M*) in various media were degassed at 0.02 mm by three freeze–pump–thaw cycles and sealed. The 313-nm Hg line was isolated using a Pyrex filter sleeve and a 1-cm path of 0.002 *M* aqueous K_2CrO_4. Valerophenone (0.1 *M*) in benzene was used as actinometer (Φ disappearance = 0.33).[9] Nitrobenzene λ_{max} (266 nm) was used to monitor nitrobenzene disappearance. Actinometer solutions were analyzed by gas chromatography using *n*-dodecane as internal standard. Our quantum yield for the disappearance of nitrobenzene in 50% 2-propanol-water containing 6 *M* HCl is 0.15 ± 0.02, which agrees with the value obtained by Hurley and Testa ($\Phi = 0.16 \pm 0.03$).[4] Quantum yield determinations on duplicate samples in the same run agreed to within 5%, while results for separate runs agreed to within 10%

Product Analyses. Nitrobenzene (308 mg, 2.5 mmol) was dissolved in 2-propanol (125 ml) and diluted to 250 ml with 12 *M* aqueous HCl. Irradiation of the solution under N_2 for 30 min gave a clear amber solution which was allowed to stand in the dark for 4 hr.[10-12] Work-up was performed by removing 2-propanol

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(2) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966).

(3) R. L. Letsinger and G. G. Wubbels, *ibid.*, **88**, 5041 (1966).

(4) R. Hurley and A. C. Testa, *ibid.*, **89**, 6917 (1967).

(5) J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

(6) M. A. Paul and F. A. Long, *Chem. Rev.*, 57, 1 (1957).

(7) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 1949 (1968).

(8) G. H. Coleman, C. H. McCloskey and F. T. Stuart, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 955, p 668.

(9) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5898 (1968).

(10) Spectra of diluted aliquots showed a shift of λ_{max} from 260 nm ($A = 0.82$) to 290 ($A = 0.11$) and 244 nm ($A = 0.69$) after 30 min of irradiation. Further irradiation of one sample caused slow loss of

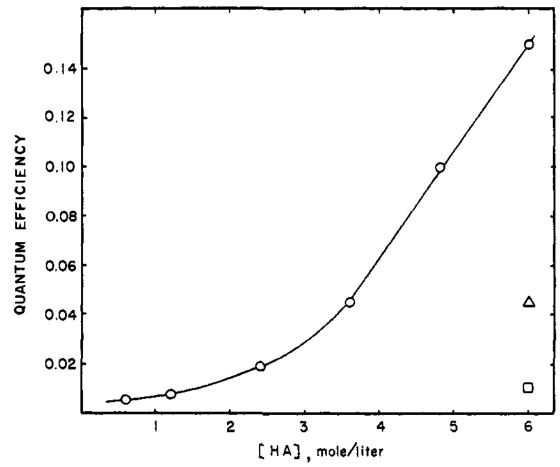


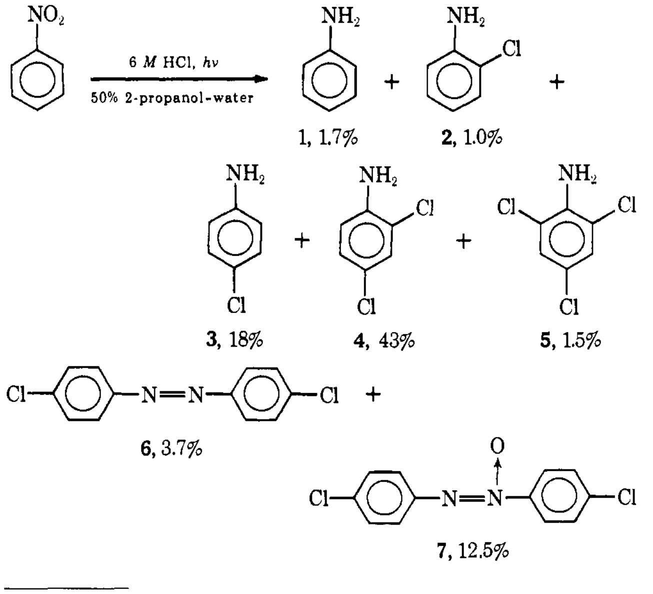
Figure 1. Quantum efficiency of nitrobenzene disappearance at 313 nm in 50% 2-propanol–water containing varying amounts of acids: HCl (○); 3.6 *M* HCl + 2.4 *M* H_2SO_4 (△); 6.0 *M* H_2SO_4 (□).

(75 ml) *in vacuo*, neutralizing the HCl (to pH 6), and extracting with ether. The concentrated extract was analyzed by gas chromatography. Product identities were established by peak enhancements with authentic samples on two different columns.

The dark reaction of nitrosobenzene was performed by dissolving nitrosobenzene (268 mg, 2.5 mmol) in 2-propanol (125 ml) under N_2 and adding 12 *M* aqueous HCl (125 ml). The blue-green of the nitroso compound was replaced instantaneously by orange upon addition of the HCl. Standing for 4 hr at room temperature gave a clear yellow solution. Work-up and analysis were performed by the same methods used for the photoreaction.

Results

Irradiation of nitrobenzene in 50% 2-propanol–water containing 6 *M* HCl gives a complex mixture of products. The major product, 2,4-dichloroaniline (43%), and most of the other products are reduced by an average of two electrons from nitrobenzene. Thus nitrosobenzene appeared attractive as a reaction intermediate, since it is known to undergo conversion to chloroanilines in the dark in the presence of HCl.[13]



1, 1.7%

2, 1.0%

3, 18%

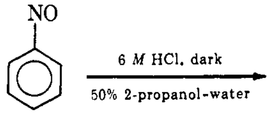
4, 43%

5, 1.5%

6, 3.7%

7, 12.5%

Indeed, nitrosobenzene reacted in the dark in 50% 2-propanol–water containing 6 *M* HCl to give a product



1, 0%; 2, 1.0%; 3, 7.3%; 4, 46.4%; 5, 4.9%; 6, 4.8%; 7, 18.2%

mixture closely resembling the mixture of photoproducts. Comparison of product yields for the photolytic and dark reactions reveals some small differences. One difference lies in the generally greater amounts of reduced products, *e.g.*, **3**, observed for the photoreaction. That this did not result from photodechlorination of the chloroaniline products[14] was shown by a control experiment in which unchanged 2,4,6-trichloroaniline was recovered (91%) after irradiation for 30 min in 50% 2-propanol–water containing 6 *M* HCl. No trace of 2,4-dichloroaniline was observed by gas chromatography.

That acetone was produced photochemically in a quantity approximately equivalent to that of reacted nitrobenzene was shown using nmr spectroscopy. A solution of nitrobenzene (0.1 *M*) in 50% 2-propanol–water containing 6 *M* HCl was irradiated in an nmr tube using a Pyrex filter. The nmr spectrum of the irradiated solution showed the acetone singlet at δ 3.08, coincident with the inner peak of the downfield ^{13}C satellites of the 2-propanol methyl doublet. Comparison of the acetone signal intensity with those of standard solutions revealed that the acetone concentration at completion of the photoreaction was 0.11 ± 0.02 *M* (110 ± 20%).

Quantum yield measurements were made using solutions of nitrobenzene in 50% 2-propanol–water containing varying amounts of different reagents. The variation in quantum yield of nitrobenzene disappearance with HCl concentration (Figure 1) agrees with that observed by Hurley and Testa.[4] The results show that increasing amounts of HCl (especially at concentrations above 3 *M*) cause substantial increases in efficiency. However, when sulfuric acid replaces hydrochloric acid (Figure 1), the quantum yields fall in proportion to the amount of HCl replaced. Thus, the efficiency of nitrobenzene disappearance in the presence of 3.6 *M* HCl–2.4 *M* H_2SO_4 (Φ = 0.045) is indistinguishable from that in 3.6 *M* HCl (Φ = 0.045) and the efficiency in the absence of acid ($\Phi \sim$ 0.005) is increased only slightly by the presence of 6 *M* H_2SO_4 (Φ = 0.011). These findings indicate that the enhancement of efficiency by HCl must involve more than just acid catalysis.[4] Indeed, chloride ion must play an essential role in the reaction.

Further evidence concerning the roles of hydrogen ion and chloride ion was gained by quantum yield measurements using LiCl–HCl mixtures in 50% 2-propanol–water (Figure 2). Under conditions where chloride ion concentration is maintained at 6 *M* and proton concentration is varied from 0 to 6 *M*, the efficiency remains constant (Φ = 0.15) from 0.05 to 6.0 *M*

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product absorption. Standing in the dark for 4 hr caused a shift of product peaks to 300 nm (A = 0.13) and 245 (A = 0.75). These spectral changes are consistent with those expected if *N*-*p*-chlorophenylhydroxylamine were the major product on cessation of irradiation and underwent slow conversion in the dark to 2,4-dichloroaniline.[11,12]

(11) Uv spectra of *N*-phenylhydroxylamine and chloroanilines were taken from "Organic Electronic Spectral Data," Vol. I–III, Interscience, New York, N. Y., 1959, 1960, 1966.

(12) For a report of the dark reaction of *N*-phenylhydroxylamine with HCl giving *o*- and *p*-chloroanilines, see H. E. Heller, E. D. Hughes, and C. K. Ingold, *Nature (London)*, **168**, 909 (1951).

(13) E. Bamberger, H. Busdorf, and B. Szolayski, *Ber.*, 32, 210 (1899).

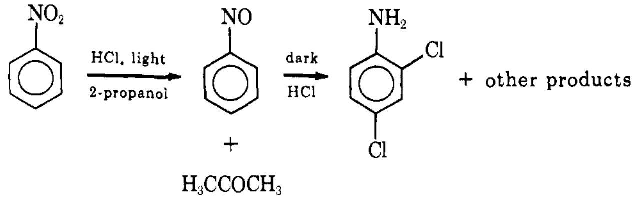
(14) T. Latowski, *Z. Naturforsch. A*, 23, 1127 (1968).

hydrogen ion concentration.[15] Below 0.05 *M* hydrogen ion concentration, efficiency falls rapidly. This finding indicates that acid catalysis is involved in the reaction, but that at high chloride ion concentration, the solution need not be strongly acidic in order for efficient reaction to occur.

Discussion

On the ground that nitrosobenzene undergoes dark conversion to the observed photoproducts when placed in the photoreaction medium, we propose Scheme I for the overall reaction.

Scheme I



Though the rates and mechanisms of the secondary reactions proceeding from the nitroso intermediate have not been studied,[16] we observed very rapid disappearance of the nitroso chromophore when nitrosobenzene in 2-propanol was treated with HCl. A second intermediate, probably *N*-*p*-chlorophenylhydroxylamine,[10] having uv absorption characteristics similar to the chloroaniline products was observed spectrally. Though we feel that the reactions leading from nitrosobenzene to products are largely nonphotochemical, we cannot exclude the possibility that appreciable photoreduction takes place at the nitroso stage[17] in competition with the dark reaction with HCl. The acetone yield (110 ± 20%) would permit this conclusion. Partial photoreduction of nitrosobenzene would account for the decreased yield of **5** and increased yield of **3** in the nitrosobenzene photoreaction relative to their yields in the nitrosobenzene dark reaction.

The lower yields of dimeric products **6** and **7** from the nitrobenzene photoreaction compared with their yields from the nitrosobenzene dark reaction may be related to the lower concentration of monomeric intermediates during the former reaction.

It is clear from the product analyses that little, if any, ring attack by chloride ion need occur in the photochemical step in order to rationalize the products. That is, if *o*- or *p*-chloronitrosobenzene were formed, 2,4,6-trichloroaniline would be the major product of its subsequent dark reaction with HCl.[18] Thus, the major photoreaction in 50% 2-propanol–water containing 6 *M* HCl appears to be photoreduction of nitrobenzene to nitrosobenzene.

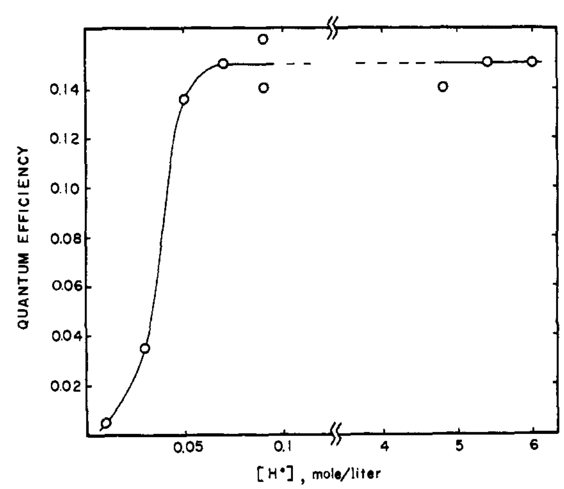


Figure 2. Quantum efficiency of nitrobenzene disappearance at 313 nm in 50% 2-propanol–water containing mixtures of HCl and LiCl such that [HCl] + [LiCl] = 6 *M*.

Hurley and Testa[4] suggested the following mechanism (eq 1–4) for the photoreaction in 50% 2-propanol–water in the presence of HCl.

$$^3PhNO_2 + H_3CCHOHCH_3 \longrightarrow PhNO_2H\cdot + H_3C\dot{C}OHCH_3 \qquad (1)$$

$$^3PhNO_2 + H^+ \longrightarrow {}^3PhNO_2H^+ \qquad (2)$$

$$^3PhNO_2H^+ + H_3CCHOHCH_3 \longrightarrow PhNO_2H\cdot + H_3C\dot{C}OHCH_3 + H^+ \qquad (3)$$

$$^3PhNO_2H^+ + Cl^- \longrightarrow \text{chloroanilines} \qquad (4)$$

The fact that sulfuric acid, a highly dissociated acid, does not cause catalysis vitiates the suggestion that acid catalysis (eq 2 and 3) accounts for the enhancement of quantum efficiency by HCl.[4] The absence of appreciable amounts of 2,4,6-trichloroaniline among the reaction products suggests that eq 4, ring attack by chloride ion, does not occur to an appreciable extent (*vide supra*).

Our consideration of mechanisms for the photoreaction has been guided by a well-supported conclusion that the reactive excited state is n,π^* in nature. That it probably is of triplet multiplicity[7] has no serious mechanistic implications. Though photoreduction of nitrobenzene by amines has been proposed to involve a $^3\pi,\pi^*$ state,[16a] we believe the weight of spectroscopic[19] and photochemical[7,20] evidence indicates that the lowest excited state in both singlet and triplet manifolds is n,π^*. The mechanism for HCl-catalyzed photoreduction shown in Scheme II is consistent with the expected electrophilic character of n,π^* photoexcited nitrobenzene and with our experimental findings and those of Hurley and Testa.[4]

The major feature of the mechanism may be seen by considering eq 6, 8, and 10. Chloride ion provides oxidation–reduction catalysis and the proton provides acid catalysis for the production of $PhNO_2H\cdot$ and $H_3C\dot{C}OHCH_3$ from $PhNO_2^*$ and $H_3CCHOHCH_3$. The secondary reactions (eq 11–13) are not justified by our results but have been examined using pulse radiolysis

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(15) Mixtures of LiCl–HCl in 50% 2-propanol–water in which total electrolyte concentration was 6 *M* were immiscible in the range 0.1 *M* < HCl > 4.5 *M* but were miscible at the extremes of the range. The heterogeneity precluded quantum yield measurements using mixtures in the immiscible range.

(16) It is apparent from the product analyses that considerable transfer of reducing equivalents between reacting intermediates occurs in the course of both photochemical and dark reactions. Mechanisms for such transfers in similar systems have been proposed; see ref 12 and (a) J. A. Barltrop and N. J. Bunce, *J. Chem. Soc. C*, 1467 (1968); (b) D. Kolb, N. Wirths, and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, 73, 148 (1969).

(17) Photoreduction of nitrosobenzene by 2-propanol giving *N*-phenylhydroxylamine has been reported by K. Pak and A. C. Testa, *J. Phys. Chem*,. 76, 1087 (1972).

(18) G. G. Wubbels, unpublished observations.

(19) For leading references see (a) M. Godfrey and J. N. Murrell, *Proc. Roy. Soc. Ser. A*, **278**, 71 (1964); (b) H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part I, H. Feuer, Ed., Interscience, New York, N. Y., 1969, p 167.

(20) (a) Reference 19b, Chapter 4; (b) W. Trotter and A. C. Testa, *J. Amer. Chem. Soc.*, 90, 7044 (1968).

Scheme II

$$\mathrm{PhNO_2^* \longrightarrow PhNO_2} \qquad (5)$$

$$\mathrm{PhNO_2^* + Cl^- \longrightarrow [PhNO_2\cdot^-, Cl\cdot]} \qquad (6)$$

$$[PhNO_2\cdot^-, Cl\cdot] \longrightarrow PhNO_2 + Cl^- \qquad (7)$$

$$\mathrm{[PhNO_2\cdot^-, Cl\cdot] + H^+ \longrightarrow [PhNO_2H\cdot, Cl\cdot]} \qquad (8)$$

$$\mathrm{[PhNO_2H\cdot, Cl\cdot] \longrightarrow PhNO_2 + H^+ + Cl^-} \qquad (9)$$

$$\mathrm{[PhNO_2H\cdot, Cl\cdot] + H_3CCHOHCH_3 \longrightarrow PhNO_2H\cdot + HCl + H_3C\dot{C}OHCH_3} \qquad (10)$$

$$\mathrm{H_3C\dot{C}OHCH_3 + PhNO_2 \longrightarrow H_3CCOCH_3 + PhNO_2H\cdot} \qquad (11)$$

$$\mathrm{2PhNO_2H\cdot \longrightarrow PhNO_2 + PhNO_2H_2} \qquad (12)$$

$$\mathrm{PhNO_2H_2 + H^+ \longrightarrow PhNO + H_2O + H^+} \qquad (13)$$

techniques by Henglein and coworkers.[21] Their findings indicate that under acidic conditions, production of nitrosobenzene and acetone from $\mathrm{PhNO_2H\cdot}$, $\mathrm{PhNO_2}$, and $\mathrm{H_3C\dot{C}OHCH_3}$ by the route shown would be rapid.

Equation 6 involving electron transfer from chloride ion to the electron hole on the nitro oxygen created by n,π^* excitation would be expected to occur at a rate near the diffusion limit if exothermic.[22,23] Thus eq 6 might be expected to compete well with rapid decay ($k \sim 10^9$ $\mathrm{sec^{-1}}$) of $\mathrm{PhNO_2^*}$ (eq 5).

The geminate radical pair formed by eq 6 could decay to starting materials by reversal of electron transfer (eq 7) or undergo a competitive sequence of reactions initiated by protonation (eq 8). The data in Figure 2 show that the quantum efficiency is dependent on a base which is about half protonated at $[\mathrm{H^+}] = 0.04$ *M* in the presence of 6 *M* LiCl. The pK_a of $\mathrm{PhNO_2H\cdot}$ has been reported to be 3.2.[21a] Since charge-transfer complexing of $\mathrm{PhNO_2H\cdot}$ with a chlorine atom would be expected to increase acidity, the species $[\mathrm{PhNO_2\cdot^-, Cl\cdot}]$ is an attractive possibility for the base in question.

That protonation of the complexed nitrobenzene anion radical should cause an increase in efficiency may be understood by considering the partitioning of $[\mathrm{PhNO_2\cdot^-, Cl\cdot}]$ between eq 7 and 14, and of $[\mathrm{PhNO_2H\cdot}$, $\mathrm{Cl\cdot}]$ between eq 9 and 10. Reversal of electron transfer (eq 7 or 9) would be more facile for $[\mathrm{PhNO_2\cdot^-, Cl\cdot}]$ than for $[\mathrm{PhNO_2H\cdot, Cl\cdot}]$ since $\mathrm{PhNO_2H^+}$ would be more electrophilic than $\mathrm{PhNO_2}$. For the same reason, the chlorine atom of $[\mathrm{PhNO_2H\cdot, Cl\cdot}]$ would be more electrophilic toward 2-propanol than that in $[\mathrm{PhNO_2\cdot^-}$, $\mathrm{Cl\cdot}]$ (*cf.* eq 10 and 14).

$$\mathrm{[PhNO_2\cdot^-, Cl\cdot] + H_3CCHOHCH_3 \longrightarrow PhNO_2\cdot^- + HCl + H_3C\dot{C}OHCH_3} \qquad (14)$$

Hurley and Testa[4] reported a decrease in efficiency of nitrobenzene disappearance in 2-propanol–water containing 6 *M* HCl when 2-propanol concentration was reduced below 25%. Thus a reaction with 2-propanol competitive with deactivation of the excited state (or intermediates derived therefrom) must occur in the mechanism. This finding is accommodated by eq 9 and 10. In the absence of 2-propanol the protonated radical pair may revert to starting materials (eq 9). In the presence of increasing concentrations of 2-propanol, an increasing fraction of the radical pair reacts productively in the competitive hydrogen abstraction process (eq 10). Apparently the intermediate reacts completely *via* eq 10 in 25% 2-propanol since the efficiency in 50% 2-propanol is unchanged from that in 25% 2-propanol.[4]

The absence of catalysis of photoreduction by sulfuric acid is a particularly striking result. This finding may be rationalized by the proposed mechanism since bisulfate ion would be expected to undergo one-electron oxidation in eq 5 with much greater difficulty than chloride ion. Justification for this view is found in the radiolysis literature. Rate constants for electron abstraction by the hydroxyl radical from chloride ion and from bisulfate ion have been reported to be 4×10^9 [24] and 8×10^5 $M^{-1}\,\mathrm{sec^{-1}}$,[25] respectively. The results in Figure 1 also show that $\mathrm{H_2SO_4}$ does not reduce the efficiency of photoexcited nitrobenzene reaction with HCl and 2-propanol. Since participation by bisulfate in eq 5 and 6 would lead to quenching, nonproductive electron transfer from bisulfate must not occur.

Several steps in the proposed mechanism have analogies in the literature. Cohen has studied photoreduction of ^{3}n,π^* aromatic ketones by amines[23] and sulfides[26] and has suggested electron transfer from heteroatom nonbonding orbitals as the primary process. Irradiation in the (ground state) charge-transfer band of complexes of ethers with nitrobenzenes was proposed by Briegleb and Lind[27] on the basis of esr evidence to cause radical ion pair formation. Photosubstitution reactions of nitroanisoles are quenched by chloride,[28] bromide,[28] and iodide[29] ions. However, since the excited states of nitroanisoles may be π,π^*, the quenching may involve nucleophilic ring attack rather than electron transfer.

The state of the chlorine atom intermediate is uncertain, but it is unlikely that free chlorine atoms exist. Chlorine atoms form adducts with chloride ion (eq 15)

$$\mathrm{Cl\cdot + Cl^- \longrightarrow Cl_2\cdot^-} \qquad (15)$$

at the diffusion rate.[30] Thus hydrogen abstraction from 2-propanol involves either eq 10 or the sequence of steps in eq 16 and 17. Regardless of the state of the

$$\mathrm{[PhNO_2H\cdot, Cl\cdot] + Cl^- \longrightarrow Cl_2\cdot^- + PhNO_2H\cdot} \qquad (16)$$

$$\mathrm{Cl_2\cdot^- + H_3CCHOHCH_3 \longrightarrow Cl^- + HCl + H_3C\dot{C}OHCH_3} \qquad (17)$$

chlorine atom, the reaction with 2-propanol would be expected to be sufficiently rapid to compete with reversion of $[\mathrm{PhNO_2H\cdot, Cl\cdot}]$ to starting materials (eq 9). In support of this contention, Langmuir and Hayon[30] report a rate constant of $1.4 \pm 0.2 \times 10^8$ $M^{-1}\,\mathrm{sec^{-1}}$ for eq 17 at *p*H 1.1.

Turning to the general question of why the catalysis

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(21) (a) K. D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 70, 862 (1966); (b) W. Grunbein, A. Foytik, and A. Henglein, *Monatsh. Chem.*, **101**, 1243 (1970).

(22) Using $\mathcal{E}^\circ$ for $\mathrm{2Cl^- = 2e^- + Cl_{2(g)}}$ and ΔH for $\mathrm{Cl_{2(g)} = 2Cl\cdot}$, the energy required for the process $\mathrm{Cl^-(aq) = Cl\cdot(g) + e^-}$ may be estimated to be about 60 kcal/mol. E_T of nitrobenzene is reported by Lewis and Kasha [*J. Amer. Chem. Soc.*, **66**, 2100 (1944)] to be 60 kcal/mol. Since the intensity and wavelength of the nitrobenzene λ_{max} undergo only slight changes attributable to a general solvent effect with the addition of HCl, we believe that a ground-state complex of $\mathrm{PhNO_2}$ and Cl^- is probably not involved in the excitation.

(23) Rate constants for electron transfer from amines to ^{3}n,π^* benzophenone of $\sim 10^8$ $M^{-1}\,\mathrm{sec^{-1}}$ have been reported by S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971).

(24) M. Burton and K. C. Kurien, *J. Phys. Chem.*, **63**, 899 (1959); M. Anbar and J. K. Thomas, *ibid.*, **68**, 3829 (1964).

(25) E. Heckel, A. Henglein, and G. Beck, *Ber. Bunsenges. Phys. Chem.*, 70, 149 (1966).

(26) J. Guttenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969).

(27) G. Briegleb and G. Lind, *Z. Naturforsch. A*, **23**, 1747 (1968).

(28) R. O. DeJongh and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **87**, 1327 (1968).

(29) R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969).

(30) M. E. Langmuir and E. Hayon, *J. Phys. Chem.*, **71**, 3808 (1967).

by HCl occurs in this system, we believe the explanation resides in the relative rates of hydrogen abstraction from 2-propanol *vs.* electron abstraction from chloride ion by photoexcited nitrobenzene. Hurley and Testa[7] suggested that the excited state is short-lived ($\tau \sim 10^{-9}$ sec) and that direct hydrogen abstraction from 2-propanol ($k \sim 1 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ by analogy to results with benzophenone[31]) competes poorly with deactivation. Electron transfer from chloride ion would be expected to occur much more rapidly (*vide supra*), causing interception of a greater proportion of excited molecules. Following electron transfer and protonation, the efficiency depends upon partitioning between the competing reactions shown in eq 9 and 10. This partitioning depends on the reactivity of the inorganic radical toward 2-propanol, toward the odd electron on the organic radical, and on the ability of the radical pair to dissipate energy. Each of these factors must be considered in predicting whether similar forms of catalysis would occur with other mineral acids or salts and other aromatic compounds.

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

Reactions of π Sulfuranes (Ylides) with Aromatic Carbonium Ions

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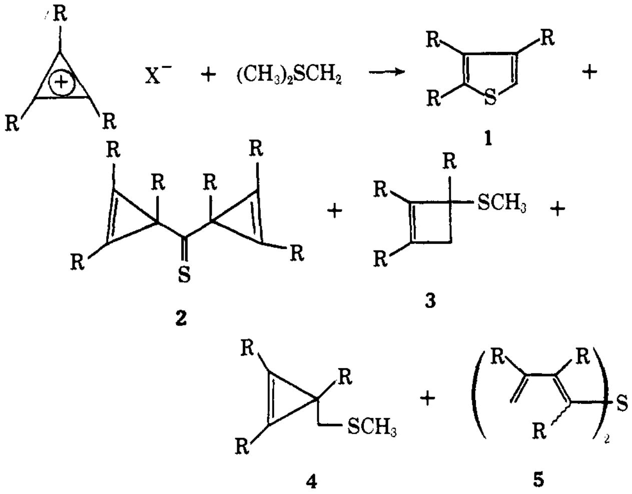
Abstract: The first observation of the use of sulfur ylides as a C–S transfer agent is reported. Reaction of triphenylcyclopropenium bromide with dimethylsulfonium methylide produced a 1.7:1.0 mixture of bis(1,2,3-triphenylcyclopropenyl) thioketone and 2,3,4-triphenylthiophene. The thioketone was characterized by its photolytic fragmentation to hexaphenylbenzene, presumably *via* hexaphenylquadricyclanthione. This reaction represents the first photochemical dethiocarbonylation. The reaction of trimethylcyclopropenium fluoroborate yielded 2,3,4-trimethylthiophene and ethane as the major products. These results suggest the intermediacy of a σ sulfurane—a species in which sulfur expanded its valence shell to ten electrons by formation of four σ bonds. The reaction is discussed in terms of the conversion of a π sulfurane into a σ sulfurane—a heterovinylcyclopropene rearrangement. σ sulfuranes similar to that postulated as intermediates in thiophene formation were generated by the treatment of triarylsulfonium salts with 2,2′-dilithiobiphenyl. Attempts to extend the C–S transfer reaction to tropylium fluoroborate led to heptafulvene instead.

The generation of nonclassical carbonium ions in strongly basic media as a potential route to strained hydrocarbons such as tetrahedrane prompted our investigation of the reaction of dimethylsulfonium methylide with cyclopropenium cations.[3] In the course of these studies, we discovered a novel new reaction indicative of π sulfurane intermediates.[4] The potential utility of σ sulfuranes in organic synthesis prompted our exploration of this reaction in detail and examination of related systems.[5]

Results and Discussion

The addition of triphenylcyclopropenium bromide[6] to a solution of dimethylsulfonium methylide[7] in THF led to a 1:1.7 mixture of two compounds, 2,3,4-triphenylthiophene (**1a**, mp 215–216°) and bis(1,2,3-triphenylcyclopropenyl) thioketone (**2a**, mp 198–200°), in 59% yield (see Scheme I). The structure of the thiophene was suggested by its mass spectrum with a molecular ion at *m/e* 312 and the appropriate M + 1 and M + 2 peaks for a single sulfur, its ultraviolet spectrum with

Scheme I. Reaction of Cyclopropenium Salts with Dimethylsulfonium Methylide



a, R = Ph; X = Br
b, R = CH_3; X = BF_4

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[2] National Institutes of Health Predoctoral Fellow.

[3] The decompositions of *p*-toluenesulfonylhydrazones in basic alcoholic solvents represent examples of such reactions. See R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967); W. Kirmse, G. Arend, and R. Siegfried, *Angew. Chem.*, **82**, 174 (1970).

[4] A σ sulfurane is defined to be a decet sulfur species possessing four σ bonds. Such species have been postulated to be intermediates in a variety of reactions. See (a) V. Franzen and C. Mertz, *Angew. Chem.*, **72**, 416 (1960); (b) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961); (c) J. Bornstein, J. E. Shields, and J. H. Supple, *J. Org. Chem.*, **32**, 1499 (1967); (d) B. M. Trost, R. W. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969); (e) W. A. Sheppard, *ibid.*, **93**, 5597 (1971); (f) B. M. Trost and R. W. LaRochelle, *ibid.*, **93**, 6077 (1971); (g) G. Wittig and H. Fritz, *Justus Liebigs Ann. Chem.*, **577**, 39 (1952).

[5] For a preliminary communication of a portion of this work, see B. M. Trost and R. C. Atkins, *Tetrahedron Lett.*, 1225 (1968).

[6] R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958).

[7] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).