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PHOTOCHEMICAL STABILIZATION OF ARYLDIAZONIUM SALTS BY CROWN ETHER COMPLEXATION[1]

Richard A. Bartsch*, Neil F. Haddock, and Douglas W. McCann
Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

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Crown ether complexes of aryldiazonium ions exhibit markedly enhanced thermal stability relative to the corresponding uncomplexed salts.[2] Thus, the thermal decomposition (Schiemann reaction) of p-*tert*-butylbenzenediazonium fluoroborate in 1,2-dichloroethane is retarded by the presence of 18-crown-6, dicyclohexyl-18-crown-6, and dibenzo-18-crown-6. Kinetic studies demonstrate that the uncomplexed diazonium fluoroborate decomposes at least one hundred times faster than the crown ether-complexed salt.[2]

Somewhat less familiar than the thermal Schiemann reaction is the photochemical decomposition of aryldiazonium tetrafluoroborates and hexafluorophosphates.[3-7] In several instances, the photochemical Schiemann reaction produces considerably higher yields of ring fluorinated aromatic and heteroaromatic compounds than result from the analogous thermal process.

In one investigation of the photochemical Schiemann reaction, Petterson and coworkers[3] irradiated solid films of aryldiazonium tetrafluoroborates and hexafluorophosphates which had been deposited on the walls of borosilicate glass vessels. Using a Rayonet photochemical reactor and 3500 Å lamps, synthetically useful yields of fluoroaromatic compounds were obtained. Since crystalline one-to-one complexes of aryldiazonium fluoroborates and crown ethers may be readily prepared,[2,8] we undertook an investigation of possible photochemical stabilization of aryldiazonium salts by crown ether complexation.

Acetone solutions of phenyldiazonium fluoroborate, 1, itself or in the presence of polyethers were evaporated *in vacuo* depositing films on the inner surface of a borosilicate glass tube. The tube was placed in a Rayonet Model RPR or RS photochemical reactor. To the tube was attached a condenser (cooling fluid at -5°C) and to the condenser, a gas buret. A corresponding empty tube was employed to correct gas volumes for thermal expansion due to heating in the photochemical reactor. After irradiation, the contents of the reaction tube were extracted with ether and analyzed by gas chromatography.[9] Yields of benzene, fluorobenzene, and evolved gas are recorded in the Table. Rates of gas evolution are illustrated in the Figure. Although no effort was made to identify the evolved gas, it was clearly evident that one component was boron trifluoride (fuming in air with deposition of boric acid).

TABLE. Products from the Photolysis of Phenyldiazonium Tetrafluoroborate

Entry	Rayonet Lamps (Å)	Polyether^a	Reaction Period (Min.)	Reaction Temperature (°C)	Gas Evolved (Equiv.)^b	Fluorobenzene Yield (%)^b	Benzene Yield (%)^b
1^c	3500	None	1100-1400	40	1.9-2.0	73-80	Trace^d
2^e	3000	None	1300	33	1.2	56	Trace
3^e	2537	None	1300	33	0.8	34	Trace
4^f	3500	18-Crown-6	1100-1200	40	0.2^g	4	18-23
5	None	18-Crown-6	1400	40	0^g	Trace	Trace
6^e	3000	18-Crown-6	1300	33	0^g	7	14
7^e	2537	18-Crown-6	1300	33	0.2^g	7	13
8	3500	15-Crown-5	1400	40	0.9	27	26
9	3500	Triglyme	1200	40	1.1	25	32

[a] [Polyether]/[$\underline{1}$] = 1.0. [b] Based upon initial $\underline{1}$. [c] Triplicate runs. [d] Less than 1%.

[e] Pyrex reaction tube. [f] Duplicate runs. [g] Uncertainty = ± 0.1.

The data recorded in Entry 1 of the Table demonstrates that solid films of $\underline{1}$ are converted into essentially quantitative yields of fluorobenzene, nitrogen, and boron trifluoride by photolysis using 3500 Å Rayonet lamps (Equation). The decrease in fluorobenzene yields when

$$\underset{\underline{1}}{C_6H_5N_2{}^+BF_4{}^-} \xrightarrow{3500\ \text{Å}} C_6H_5F + N_2 + BF_3 \qquad \text{(Equation)}$$

light of shorter wavelengths was utilized (Entries 2 and 3) has previously been noted by Petterson and coworkers.[3]

When a one-to-one complex of $\underline{1}$ and 18-crown-6 was irradiated (Entries 4, 6, and 7), yields of fluorobenzene and gaseous products plummet. A dramatic effect of complexation by 18-crown-6

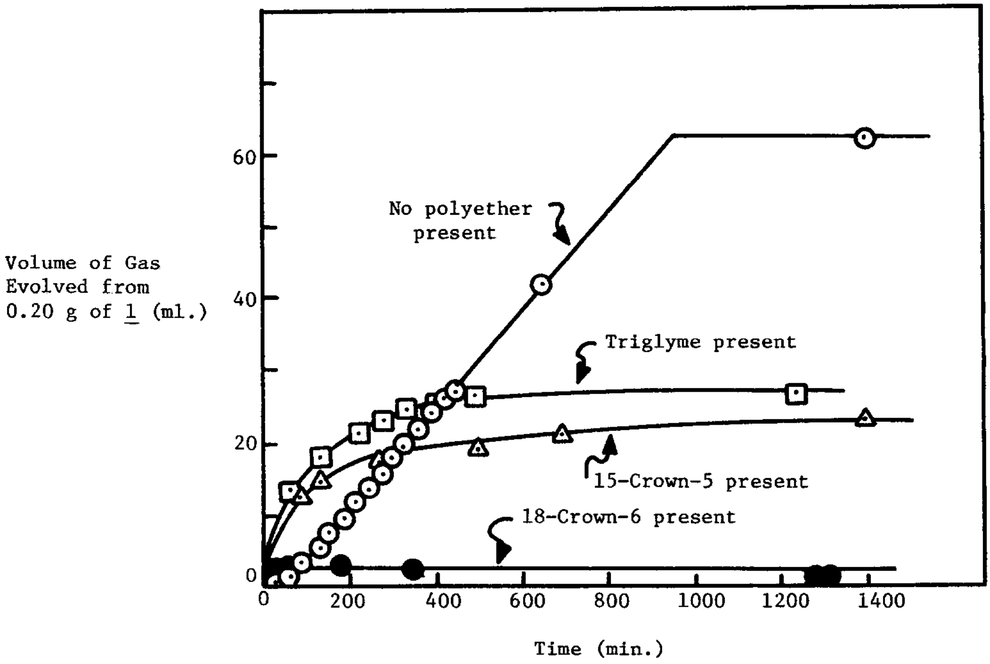

FIGURE. Rate of Gas Evolution in the Photolysis of Benzenediazonium Tetrafluoroborate with 3500 Å Lamps

upon the rate of gas evolution during irradiation with 3500 Å lamps is shown in the Figure. In the absence of light, no products were formed from the complex of 1 and 18-crown-6 (Entry 5).

In a separate experiment, the complex of 1 and 18-crown-6 was photolyzed under the conditions listed in Entry 4. At the end of reaction period, distilled water was added to reaction tube. After filtration to remove a small amount of tarry material, the filtrate was poured into an alkaline solution of 2-naphthol. From gravimetric analysis of the resultant orange azo compound, it was calculated that 55% of the diazonium salt remained at the end of the irradiation period. Thus, the function of 18-crown-6 is photochemical stabilization of 1 and not merely diversion of a photo-intermediate to form other products.

Effects of two other polyethers, 15-crown-5 and triglyme, upon the products derived from the photolysis of 1 were also examined. For the former, the crown ether cavity is too small to accommodate aryldiazonium ions.[2,10] In the latter, the cyclic polyether structure is absent. Therefore, even though both compounds are polyethers, neither should be able to provide the specific complexation of the photochemical stabilization of 1 observed with 18-crown-6. As may be seen in the Figure, 15-crown-5 and triglyme actually accelerate the rate of gaseous product formation in the photolysis of 1. Comparison of Entries 4, 8, and 9 in the Table reveals that much higher yields of fluorobenzene and gaseous products are observed when 18-crown-6 is replaced by 15-crown-5 or triglyme.

Thus, we have demonstrated that the complexation of aryldiazonium ions with crown ethers of an appropriate size provides photochemical, as well as thermal, stabilization. Studies of the mechanism by which the photochemical stabilization is effected are in progress.

NOTES AND REFERENCES

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