The Action of Hypochlorite on Sulfanilate

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The production of azobenzene-4,4′-disulfonate (**1**) by the action of chlorine on sulfanilate in aqueous sodium carbonate, observed by Tishchenko,[1] has been repeated with the use of commercial sodium hypochlorite solution. In this highly exothermic reaction a monochloroazobenzenedisulfonate (**2**) was formed as a by-product; when the temperature was held below 10° a phenazinedisulfonate (**3**) could also be isolated.

The sodium phenazinedisulfonate was readily extracted from the mixed azo salts (**1** with 10–15% of **2**) by 0.5 *M* sodium nitrate,[2] in which they are sparingly soluble, but the composition of this residual mixture was not appreciably changed by recrystallization or by chromatographic procedures. However, the triethylammonium salts proved to be separable; that of azobenzene-4,4′-disulfonic acid was isolated by repeated crystallization from methanol, that of its chloro analog **2** by taking advantage of its greater solubility in 1-butanol and acetone.

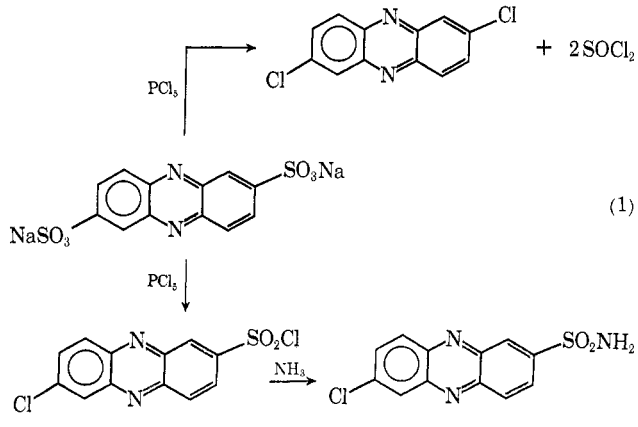
When samples of the mixed sodium azobenzenedisulfonates (**1** and **2**, freed of phenazinedisulfonate) were converted into disulfochlorides,[3,4] the products could be separated by crystallization from toluene, that from the monochloroazo compound being the more soluble.

As was to be expected, the chlorine atom in **2** was located in a position ortho to the azo group. This was supported by the infrared spectrum (in KCl) of the triethylammonium chloroazobenzenedisulfonate, which showed an absorption band at 730 cm^{-1}, not present in the corresponding chlorine-free salt; a strong band at the same wavelength was shown by 3-chloro-4-aminobenzene sulfonic acid and not by sulfanilic acid. The allocation was confirmed by synthetic evidence: oxidation of a mixture of potassium sulfanilate with 75% of an equimolar quantity of potassium 3-chloro-4-aminobenzenesulfonate with permanganate by the procedure of Laar[3] afforded a small yield of azodisulfonates containing 70% of the theoretical amount of chlorine; the disulfonanilide from this product, after purification, was shown by mixture melting point to be identical with a sample derived from the reaction of hypochlorite with sulfanilate alone.

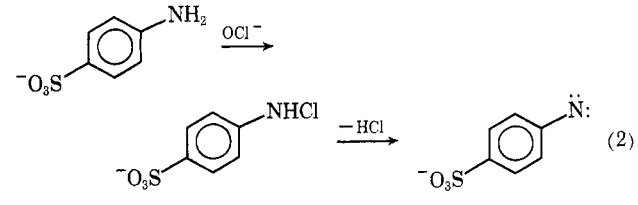
Introduction of chlorine from the hypochlorite into the carbon structure must have taken place prior to the formation of the azobenzenedisulfonic ion, for no reaction between sodium azobenzene-4,4′-disulfonate and hypochlorite could be detected, even at 25°.

The replacement of a sulfonic group by chlorine, reported in the case of benzenesulfonic acid by Meyer and Schlegel,[5] was observed to take place to a slight extent in the preparation of azobenzene-4,4′-disulfochloride, when 4-chloroazobenzene-4′-sulfochloride appeared as a more soluble by-product. The position entered by the chlorine atom was confirmed by reduction of the azo group in the corresponding sulfonanilide by stannous chloride, whereby *p*-chloroaniline, characterized as its acetyl derivative,[6] mp 178°, was obtained as the sole steam-volatile base.

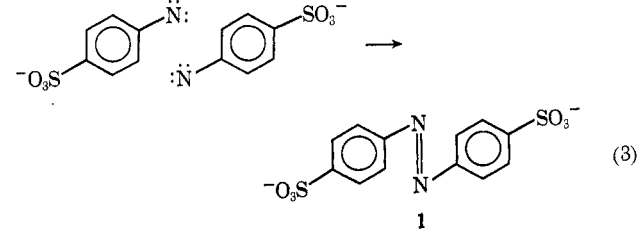
The sulfonate groups in the phenazine product **3** are in positions 2 and 7 as evidenced by the formation of the well-known 2,7-dichlorophenazine[7,8] upon treatment of the sodium salt of **3** with thionyl chloride and dimethyl formamide.[9] With phosphorus pentachloride, reaction takes place less rapidly; there is formed not only some dichlorophenazine, but also another toluene-soluble product, 2-chlorophenazine-7-sulfochloride, which on treatment with ammonia yields 2-chlorophenazine-7-sulfonamide (eq 1). Thionyl chloride was detected among the volatile components of the reaction mixture.



The reactions of sulfanilate with hypochlorite are attributable to transitory formation of nitrenes (eq 2).



The formation of azobenzenedisulfonate is pictured as a simple combination of two nitrene molecules (eq 3).



1

(1) D. V. Tishchenko, *J. Russ. Phys. Chem. Soc.*, **60**, 153 (1928).

(2) 0.5 *M* sodium acetate extracts the phenazine derivative equally well, but is less readily removable by methanol.

(3) C. Laar, *J. Prakt. Chem.*, **20**, 242 (1879).

(4) C. Laar, *Ber.*, **14**, 1928 (1881).

(5) H. Meyer and K. Schlegl, *Monatsh. Chem.*, **34**, 56 (1913); H. Meyer, *ibid.*, **36**, 719 (1915).

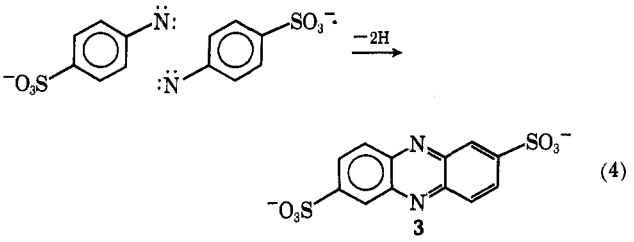
(6) N. V. Sidgwick and H. E. Rubie, *J. Chem. Soc.*, **119**, 1013 (1921).

(7) R. A. Abramovitch and B. A. Davis, *J. Chem. Soc. C*, 119 (1968); *J. Heterocycl. Chem.*, **5**, 793 (1968).

(8) The author is deeply indebted to Dr. Abramovitch for confirming the identity of this product, by means of its infrared spectrum, with a sample prepared in his laboratory by a different method.

(9) H. H. Bosshard, R. Mory, M. Schmid, and H. Zollinger, *Helv. Chim. Acta*, **42**, 1653 (1959).

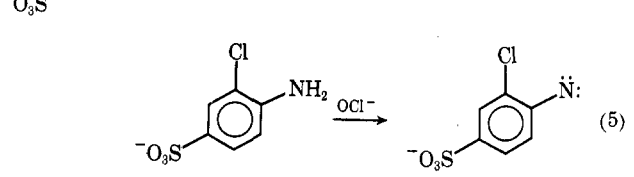
In the formation of phenazinedisulfonate, dehydrogenation is involved (eq 4). To account for the formation



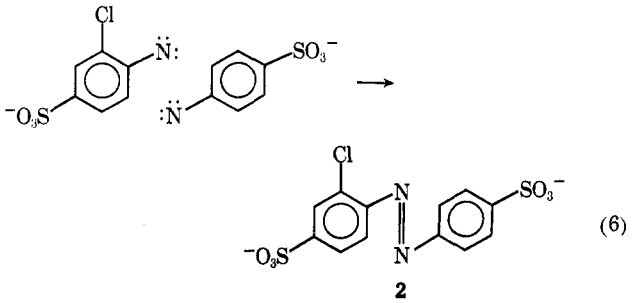
(4)

3

of the chloroazobenzenedisulfonate, migration of a chlorine atom from nitrogen to carbon (eq 5) would be followed by the coupling of the chlorinated nitrene with the chlorine-free species (eq 6).



(5)



(6)

2

Intermediary formation of nitrenes has recently been invoked to explain the mechanism of the deoxygenation of nitrosobenzene by ethyl phosphite.[10] Although reactions of this kind have not hitherto been postulated to take place in alkaline aqueous solution, their occurrence therein would be consistent with the experimental observations here reported.

Experimental Section

All melting points were observed in capillary tubes and with calibrated thermometers. In the early stages of the work the microanalyses were performed under the direction of Dr. S. M. Nagy at the Massachusetts Institute of Technology, later by the Scandinavian Microanalytical Laboratory and by the Galbraith Laboratories of Knoxville, Tenn.

Oxidation of Sulfanilate.—In a typical preparation a solution of 48 g (0.25 mol) of sulfanilic acid in 450 ml of water and enough sodium carbonate to bring the pH to 9 was chilled in an ice–salt bath. When the temperature had fallen to below 5°, 600 ml of commercial sodium hypochlorite solution (0.7 *M*, pH 12) was added dropwise, with mechanical stirring, during 2 hr, the reaction mixture being held at about 0°. The mixture was then left to stand at 3–5° for 20 hr and the orange-yellow crystals which had separated were collected, washed with small quantities of water and then with methanol, and dried (crop A, 5.9 g). The combined filtrates were concentrated under reduced pressure to 256 ml; the resulting suspension was chilled overnight at 3° and filtered. The pale brown, crystalline product was washed with 2 *M* $NaNO_3$ and then with methanol, and dried (crop B, 12.2 g). The mother liquor was concentrated to 150 ml, when NaCl had begun to separate. The solids were washed with 2 *M* $NaNO_3$ to remove NaCl, with 0.5 *M* $NaNO_3$, and then with methanol, and dried. The light red powder (25.6 g) was recrystallized from 300 ml of water, from which crop C (18.2 g) was obtained.

Silver Phenazine-2,7-disulfonate.—The first crystals collected (crop A) were washed with 0.5 *M* $NaNO_3$, but the washings yielded no phenazinedisulfonate. Crops B and C, washed with 0.5 *M* $NaNO_3$, yielded a dark solution which was concentrated to one-quarter volume and the resulting solid was washed with 2 *M* $NaNO_3$ and then with methanol, and dried (7.1 g). This product was almost completely soluble in 90 ml of 0.5 *M* $NaNO_3$; after treatment with decolorizing carbon the filtrate was acidified with 2 ml of 2 *M* HNO_3 and treated with an excess of silver nitrate solution. The canary-yellow precipitate of silver phenazinedisulfonate was washed with 0.05 *M* $AgNO_3$, then with 1:1 CH_3OH–H_2O, and dried *in vacuo* at 110°, yield 6.75 g (9.8%).

Anal. Calcd for $C_{12}H_6N_2O_6S_2Ag_2$: C, 26.0; H, 1.1; N, 5.1; S, 11.6; Ag, 39.0. Found: C, 26.1; H, 1.6; N, 5.0; S, 11.8; Ag, 38.8.

In pure water this salt forms a colloidal suspension which peptizes silver halides and passes through filter paper.

Triethylammonium Azobenzene-4,4′-disulfonate.—A portion of crop C, after being washed with $NaNO_3$ and methanol, was recrystallized from water and dried.

Anal. Found: C, 36.95; H, 2.15; Cl, 1.1; N, 7.1; S, 16.4. Calcd for $C_{12}H_7ClN_2O_6S_2Na_2$ + $8C_{12}H_8N_2O_6S_2Na_2$: C, 37.05; H, 2.08; Cl, 1.0; N, 7.2; S, 16.4. Calcd for $C_{12}H_7ClN_2O_6S_2Na_2$ + $7C_{12}H_8N_2O_6S_2Na_2$: C, 36.93; H, 2.02; Cl, 1.1; N, 7.2; S, 16.4.

The washed mixture of sodium salts crops A, B, and C was converted into the sparingly soluble calcium salts, which were then decomposed with aqueous triethylammonium carbonate. The filtrate was evaporated to dryness and the residue was repeatedly recrystallized from methanol until it melted sharply, without decomposition, at 242°. The pure salt forms flat orange-yellow prisms, readily soluble in cold methanol, markedly less so in ethanol, sparingly in propanols and butanols, and almost insoluble in acetone: uv $\lambda_{max}^{H_2O}$ 320 and 435 nm (E_{mol} 17,600 and 907, respectively).

Anal. Calcd for $C_{24}H_{40}N_4O_6S_2$: $(C_2H_5)_3N$, 37.2. Found: 36.6.

Stability of Sodium Azobenzene-4,4′-disulfonate toward Hypochlorite.—A solution of 6.5 g of the pure triethylammonium azobenzene-4,4′-disulfonate in water was decomposed with sodium carbonate and the liberated amine was volatilized under reduced pressure. The residue was diluted to 450 ml and treated with 50 ml of 0.7 *M* sodium hypochlorite at 25°. After 2 hr ammonia was added (to reduce hypochlorite). The solution was evaporated under reduced pressure at 30–35°, diluted to 500 ml, and acidified with acetic acid; to the clear solution 100 ml of 1 *M* calcium acetate was added. When cold, the crystalline calcium salt was washed with cold water and dried. The yield (4.5 g) was almost quantitative.

Anal. Calcd for $C_{12}H_8N_2O_6S_2Ca$: Ca, 10.5. Found: Ca, 10.4; Cl, 0.0.

Triethylammonium 2-Chloroazobenzene-4,4′-disulfonate.—The methanolic mother liquor from the triethylammonium azobenzene-4,4′-disulfonate was evaporated to dryness and the residue was washed with cold 1-butanol until the solvent extracted very little yellow color. The extract was evaporated to dryness under reduced pressure and the solids were washed with cold acetone until the washings were no deeper in color than a saturated solution of the pure triethylammonium azobenzene-4,4′-disulfonate in acetone. This filtrate was chilled overnight at 5°, decanted from a small amount of crystalline product, treated with charcoal, and allowed to evaporate spontaneously for 2 weeks at 5°, when fine yellow-orange needles (of the chlorine-free salt) and large, red rhombic prisms had deposited. The former were removed mechanically by gentle agitation with the mother liquor, decantation and filtration, the process being frequently repeated with the filtrates. The rhombs, which remained undisturbed, were selected manually and dried at 90°. They melted at 191° and were slightly more soluble than the chlorine-free salt in alcohols and acetone: uv $\lambda_{max}^{H_2O}$ 323 and 439 nm (E_{mol} 17,500 and 867, respectively).

(10) R. J. Sundberg, *J. Amer. Chem. Soc.*, **88**, 3781 (1966); R. J. Sundberg, R. H. Smith, Jr., and J. E. Bloor, *ibid.*, **91**, 3392 (1969); R. J. Sundberg and R. H. Smith, Jr., *J. Org. Chem.*, **36**, 295 (1971); R. J. Sundberg and C.-C. Lang, *ibid.*, **36**, 300 (1971).

Anal. Calcd for $C_{24}H_{39}ClN_4O_6S_2$: Cl, 6.1; N, 9.7; S, 11.1. Found: Cl, 6.1; N, 9.9; S, 10.9.

2-Chloroazobenzene-4,4′-disulfochloride.—Another preparation of sodium salts, similar to crop C, was converted into disulfochlorides by treatment with thionyl chloride and dimethylformamide[9] and the products were fractionally crystallized from toluene. The least soluble component was the expected azobenzene-4,4′-disulfochloride, mp 224°; on concentration the mother liquor yielded the 2-chloro derivative, slender needles from toluene, mp 174°, almost insoluble in cyclohexane.

Anal. Calcd for $C_{12}H_7Cl_3N_2O_4S_2$: Cl, 25.7; S, 15.5. Found: Cl, 25.6; S, 15.4.

4-Chloroazobenzene-4′-sulfochloride.—The mother liquor from the foregoing fraction was evaporated to dryness and the residue was washed with cyclohexane, which extracted a pale red product, fine needles, mp 127°.

Anal. Calcd for $C_{12}H_8Cl_2N_2O_2S$: C, 45.7; H, 2.5; Cl, 22.5; N, 8.9; S, 10.2. Found: C, 45.7; H, 2.5; Cl, 22.8; N, 8.8; S, 10.2.

4-Chloroazobenzene-4′-sulfonanilide.—Treatment of the above sulfochloride with aniline yielded the anilide, red-orange leaflets from methanol, mp 171°, readily soluble in acetone.

Anal. Calcd for $C_{18}H_{14}ClN_3O_2S$: C, 58.2; H, 3.8; Cl, 9.6; N, 11.3; S, 8.6. Found: C, 57.5; H, 3.7; Cl, 9.6; N, 11.4; S, 8.3.

The sodium derivative forms filamentous needles, almost insoluble in 0.05 *M* NaOH.

Replacement of One Sulfo Group in Azobenzene-4,4′-disulfochloride by Chlorine.—Pure azobenzene-4,4′-disulfochloride (3.8 g) in toluene (7 ml) was subjected under the usual conditions[9] to the action of thionyl chloride and dimethylformamide for 2 hr on the steam bath. When cool, the recovered crude starting material (3.36 g, mp 200–212°) was recrystallized from toluene, 2.65 g, mp 223°. The mother liquor was washed with water and treated with aniline; the product, purified through the sodium derivative and recrystallized, consisted of red-gold leaflets, mp 171°, 0.25 g.

Replacement of One Sulfo Group in Sodium Phenazine-2,7-disulfonate.—An intimate mixture of 6.7 g of sodium phenazinedisulfonate and 9.2 g of phosphorus pentachloride was heated in 15 ml of toluene under reflux on the steam bath for 23 hr. No gas was evolved in the reaction. The suspended solids were washed with 50 ml of toluene to extract yellow products and the combined filtrate was distilled at 25–30° under slightly reduced pressure. The presence of thionyl chloride in the distillate was demonstrated by mixing it with ice–water and aspirating the resulting sulfur dioxide into dilute permanganate, which was reduced with the formation of sulfate.

The residue from the distillation of the toluene washings was treated with concentrated aqueous ammonia; after 24 hr the mixture was shaken with dilute NaOH and the yellow washings were concentrated and acidified with acetic acid. The resulting colorless, amorphous precipitate of 2-chlorophenazine-7-sulfonamide, mp 303° with darkening, weighed 1.5 g after being washed with water and methanol. It was insoluble in water, 1-butanol, toluene, and acetic acid.

Anal. Calcd for $C_{12}H_8ClN_3O_2S$: N, 14.3; S, 10.9. Found: N, 14.3; S, 10.9.

The alkali-washed toluene solution was concentrated; the residue on recrystallization from toluene yielded 1.9 g of 2,7-dichlorophenazine, long, pale yellow needles, mp 266°, identical with the sole product (67% yield) obtained by treatment of sodium phenazinedisulfonate with thionyl chloride and dimethylformamide.

During the course of this study, many derivatives were prepared by standard methods, largely in a search for compounds which might be of aid in effecting the separation of chlorinated from unsubstituted azobenzenedisulfonates. Analyses and characterizations of these are outlined below.

Trimethylammonium azobenzene-4,4′-disulfonate was obtained as red-orange needles from ethanol, mp 267°.

Anal. Calcd for $C_{18}H_{28}N_4O_6S_2$: $(CH_3)_3N$, 25.7. Found: N, 26.1.

Pyridinium azobenzene-4,4′-disulfonate was obtained as orange needles from ethanol, mp 225°.

Anal. Calcd for $C_{22}H_{20}N_4O_6S_2$: N, 11.2. Found: N, 11.1.

Azobenzene-4,4′-disulfonamide was obtained as fine yellow needles or leaflets, appreciably soluble in acetone, almost insoluble in ethanol, insoluble in water, mp 322°, darkening only at the melting point. This compound is described in the literature as fairly readily soluble in alcohol, still solid at 300°,[11] also as charring above 250° without melting.[4]

Azobenzene-4,4′-di(sulfonyl-*N*-dimethylamine) was obtained as red-orange leaflets from dimethylformamide, mp 312°.

Anal. Calcd for $C_{16}H_{20}N_4O_4S_2$: N, 14.1. Found: N, 14.1.

Azobenzene-4,4′-di(sulfonyl-*N*-diethylamine) was obtained as long, flat, red-gold needles, mp 187° from acetone–ethanol.

Anal. Calcd for $C_{20}H_{28}N_4O_4S_2$: N, 12.4. Found: N, 12.9.

Azobenzene-4,4′-disulfonanilide was obtained as heavy red prisms from hot acetone, mp 264°, sparingly soluble in most organic liquids, insoluble in water, readily soluble in dilute alkali.

Anal. Calcd for $C_{24}H_{20}N_4O_4S_2$: N, 11.4; S, 13.0. Found: N, 11.2; S, 13.0.

Azobenzene-4,4′-di(sulfonyl-*N*-methylaniline) was obtained as long, pink needles from toluene, mp 221°.

Anal. Calcd for $C_{26}H_{24}N_4O_4S_2$: N, 10.8; Found: N, 10.7.

Barium 2-chloroazobenzene-4,4′-disulfonate was sparingly soluble in water.

Anal. Calcd for $C_{12}H_7ClN_2O_6S_2Ba$: C, 28.2; H, 1.4; Cl, 6.9; N, 5.5; S, 12.5; Ba, 26.9. Found: C, 28.2; H, 1.9; Cl, 7.1; N, 5.7; S, 11.9; Ba, 27.7.

2-Chloroazobenzene-4,4′-disulfonanilide was obtained as red needles from toluene, mp 216°, readily soluble in acetone.

Anal. Calcd for $C_{24}H_{19}ClN_4O_4S_2$: C, 54.8; H, 3.6; Cl, 6.7; N, 10.6; S, 12.2. Found: C, 55.4; H, 3.8; Cl, 6.5; N, 10.6; S, 12.2.

4-Chloroazobenzene-4′-sulfonyl-*N*-diethylamine was obtained as pale pink, slender needles from ethanol, mp 152°.

Anal. Calcd for $C_{16}H_{18}ClN_3O_2S$: C, 55.0; H, 4.6; Cl, 10.1; N, 12.0; S, 9.2. Found: C, 54.5; H, 5.2; Cl, 10.5; N, 11.9; S, 8.3.

4-Chloroazobenzene-4′-sulfonyl-*N*-methylaniline was obtained as pink prisms from acetone–methanol, mp 166°, sparingly soluble in methanol.

Anal. Calcd for $C_{19}H_{16}ClN_3O_2S$: C, 59.2; H, 4.2; Cl, 9.2; N, 10.9; S, 8.3. Found: C, 58.8; H, 4.2; Cl, 9.4; N, 10.8; S, 8.5.

Sodium Phenazine-2,7-disulfonate.—To aqueous suspensions of the silver salt, aqueous sodium chloride was added dropwise; at the equivalence point the suspended solids coagulated. Sodium carbonate solution was also effective. The filtrates, on concentration, yielded fine, pale yellow needles, readily soluble in water, sparingly in 2 *M* sodium acetate or nitrate, insoluble in methanol: uv $\lambda_{max}^{H_2O}$ (pH 1, 7, 14) 257 and 370 nm (E_{mol} 70,000 and 820, respectively).

Anal. Calcd for $C_{12}H_6N_2O_6S_2Na_2$: C, 37.6; H, 1.6; N, 7.3; S, 16.7; Na, 12.0. Found: C, 37.5; H, 1.6; N, 7.3; S, 16.8; Na, 12.0.

Potassium phenazine-2,7-disulfonate was obtained as stout prisms, containing $4H_2O$ (15%) lost at 110°.

Anal. Calcd for $C_{12}H_6N_2O_6S_2K_2$: N, 6.7; K, 18.8. Found: N, 6.7; K, 18.6.

Barium phenazine-2,7-disulfonate was a pale yellow compound whose solubility in water was 0.03% at 28°, 0.066% at 100°.

Anal. Calcd for $C_{12}H_6N_2O_6S_2Ba$: Ba, 28.8. Found: Ba, 28.4.

Triethylammonium phenazine-2,7-disulfonate was obtained as fine, pale yellow needles, mp 213°, readily soluble in methanol, less so in ethanol and 2-propanol.

Anal. Calcd for $C_{24}H_{38}N_4O_6S_2$: N, 10.3; S, 11.8. Found: N, 10.4; S, 11.8.

2-Chlorophenazine-7-sulfonanilide was obtained as light yellow leaflets from acetone, mp 215°; solution in dilute NaOH is deep orange.

Anal. Calcd for $C_{18}H_{12}ClN_3O_2S$: C, 58.6; H, 3.3; Cl, 9.6; N, 11.4; S, 8.7. Found: C, 58.4; H, 3.3; Cl, 9.5; N, 11.5; S, 8.7.

Registry No.—Hypochlorite, 14380-61-1; sulfanilate, 2906-34-5; silver phenazine-2,7-disulfonate, 31819-69-9; triethylammonium azobenzene-4,4′-disulfonate, 31819-70-2; calcium azobenzene-4,4′-disulfonate, 31819-71-3; triethylammonium 2-chloroazobenzene-4,4′-disulfonate, 31819-72-4; 2-chloroazobenzene-4,4′-disulfochloride, 31819-73-5; 4-chloroazobenzene-4′-sulfochloride, 31819-74-6; 4-chloroazobenzene-4′-sulfon-

(11) H. Limpricht, *Ber.*, **14**, 1356 (1881).

anilide, 31819-75-7; 2-chlorophenazine-7-sulfonamide, 31819-76-8; 2,7-dichlorophenazine, 3372-79-0; trimethylammonium azobenzene-4,4′-disulfonate, 3819-78-0; pyridinium azobenzene-4,4′-disulfonate, 31819-79-1; azobenzene-4,4′-di(sulfonyl-*N*-dimethylamine), 31819-80-4; azobenzene-4,4′-di(sulfonyl-*N*-diethylamine), 31819-81-5; azobenzene-4,4′-disulfonanilide, 31819-82-6; azobenzene-4,4′-di(sulfonyl-*N*-methylaniline), 31819-83-7; barium 2-chlorobenzene-4,4′-disulfonate, 31819-84-8; 2-chloroazobenzene-4,4′-disulfonanilide, 31815-05-1; 4-chloroazobenzene-4′-sulfonyl-*N*-diethylamine, 31815-06-2; 4-chloroazobenzene-4′-sulfonyl-*N*-methylaniline, 31815-07-3; sodium phenazine-2,7-disulfonate, 31815-08-4; potassium phenazine-2,7-disulfonate, 31815-09-5; barium phenazine-2,7-disulfonate, 31815-10-8; triethylammonium phenazine-2,7-disulfonate, 31815-11-9; 2-chlorophenazine-7-sulfonanilide, 31815-12-0.

Acknowledgment.—The author is grateful to Dr. J. S. Fruton for according him laboratory facilities in the Department of Biochemistry of Yale University during the early stages of this work and to the National Institutes of Health for a grant in support of the laboratory; to Dr. Sidney Farber for making it possible for this investigation to be completed in the Children's Cancer Research Foundation at the Children's Hospital Medical Center in Boston; to Dr. Johannes Meienhofer for the hospitality of his large Sephadex column and for advice in the interpretation of infrared spectra; to Mr. Roger Cavallo and Miss Kathleen Gould for uv and ir data; to Dr. Mervyn Israel for helpful advice relative to the organization of this report.

Photodifluoramination of Fluoromethane

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Photodifluoramination of alkanes with N_2F_4 at 253.7 nm involves the steps[1] shown in eq 1–5. When methane is subjected to this reaction, HCN is produced by unimolecular elimination of HF from chemically activated CH_3NF_2,[2] a system that has been used as an elimination chemical laser.[3] We report now the photodifluoramination of fluoromethane, a case which contrasts dramatically with that of methane.

$$N_2F_4 \longrightarrow 2NF_2 \quad (1)$$

$$NF_2 \xrightarrow{h\nu} NF + F \quad (2)$$

$$R\text{-}H + F \longrightarrow HF + R \quad (3)$$

$$R + NF_2(N_2F_4) \longrightarrow R - NF_2 \quad (4)$$

$$NF + NF_2 \longrightarrow N_2F_2 + F \quad (5)$$

(1) C. L. Bumgardner, E. L. Lawton, K. M. McDaniel, and H. H. Carmichael, *J. Amer. Chem. Soc.*, **92**, 1311 (1970).

(2) C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

(3) T. D. Padrick and G. C. Pimentel, *J. Chem. Phys.*, **54**, 720 (1971).

Irradiation of an equimolar mixture of CH_3F and N_2F_4 in a Pyrex vessel for 30 min at a total initial pressure of 108 Torr gave the results summarized in eq 6.

$$\begin{array}{lll} & CH_3F + N_2F_4 \xrightarrow{253.7\ nm} & \\ \text{mmoles} & 2.18 \quad 2.23 & \\ & CH_3F + FCH_2NF_2 + (FCH_2)_2 + & \\ & 0.02 \quad 2.02 \quad 0.05 & \\ & N_2F_2 + SiF_4 + N_2O + N_2 & (6) \\ & 0.99 \quad 0.55 \quad 0.27 \quad 0.10 & \end{array}$$

The reaction was monitored by quantitative mass spectrometry. Products were separated by trap-to-trap distillation and the contents of each trap were examined by mass and infrared spectrometry and by gas chromatography.

During photodifluoramination of CH_4 under these reaction conditions, significant unimolecular elimination of HF occurs from CH_3NF_2 which is vibrationally excited. However, if the FCH_2NF_2 formed as described suffers any loss of HF at all, the amount of elimination must be several orders of magnitude lower than elimination from CH_3NF_2. Mass balances indicate that 94% of the carbon introduced as CH_3F is accounted for by FCH_2NF_2 and recovered CH_3F. We conclude therefore that $(k_2/k_1)_{FCH_2NF_2} \gg (k_2/k_1)_{CH_3NF_2}$.

$$CH_3 + NF_2(N_2F_4) \longrightarrow CH_3{}^*NF_2 \begin{cases} \xrightarrow[k_2]{M} CH_3NF_2 \\ \xrightarrow[k_1]{} HCN + 2HF \end{cases}$$

The remarkable effect produced by replacing one of the C–H bonds in the above system with a C–F bond may be due to the greater capacity of a C–F bond to store excess vibrational energy.[4,5] The presence of a C–F linkage also may increase the activation energy for HF elimination across the C–N bond of a difluoramine.[6]

Formation of FCH_2CH_2F is undoubtedly due to some coupling of the FCH_2 radical intermediates, the first time this process has been observed in the photodifluoramination reaction. The higher concentration of NF_2 and N_2F_4 relative to that of the alkyl radical (R) generated in step 3 generally makes step 4 much more important than dimerization of R.

Experimental Section[7]

Caution: Tetrafluorohydrazine and derivatives should be handled with care. Operations were conducted routinely behind shields.

Photodifluoramination of Fluoromethane.—In an apparatus described previously for the photodifluoramination of methane,[1] 2.18 mmol of fluoromethane (99.0%, Matheson) and 2.23 mmol

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(5) J. A. Kerr, D. C. Phillips, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1086 (1968).

(6) A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).

(7) Proton nuclear magnetic resonance, fluorine nuclear magnetic resonance, infrared, and mass spectra were obtained using the following instruments, respectively: Varian HA-100 high-resolution spectrometer, Varian DA 60 high-resolution spectrometer, Beckman IR-5A spectrophotometer, and Consolidated Model 620 and Associated Electronics Model MS902 mass spectrometers. Nmr spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. Fluorine (^{19}F) chemical shifts (ϕ) are in parts per million relative to fluorotrichloromethane as an external reference. Proton (^1H) chemical shifts (δ) are in parts per million downfield relative to tetramethylsilane as an internal reference.