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DISULFUR DECAFLUORIDE (S_2F_{10}): A REVIEW OF THE BIOLOGICAL PROPERTIES AND OUR EXPERIMENTAL STUDIES OF THIS BREAKDOWN PRODUCT OF SF_6

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ABSTRACT

The toxicity of S_2F_{10} (disulfur decafluoride) to whole animals and to cells is discussed. The strong toxicity of S_2F_{10}, comparable to the toxicity of phosgene in some species, suggested the possible use of S_2F_{10} as a warfare agent. Exposures to as little as 0.1 ppm for 18 h have produced lung irritation in rats. Cell culture studies in our laboratory have shown S_2F_{10} to be by far the most toxic product we have so far identified in laboratory samples of electrically-decomposed SF_6. The significance of these toxicological studies for electrical utility personnel depends on (1) the presence and amount of S_2F_{10} found in actual applications and (2) the effectiveness of clean-up methods applied to faulted gas equipment.

INTRODUCTION: RELEVANCE TO SF_6-INSULATED EQUIPMENT

Although disulfur decafluoride (S_2F_{10}) has many interesting chemical and biological properties, it is, at best, a laboratory curiosity to scientists and engineers concerned with practical applications of electrical energy systems, unless it can be shown to be an actual byproduct of SF_6 decomposition (and present in "significant" amounts) in real-world electrical utility operations. If, in fact, such demonstrations are forthcoming, then issues regarding its degree of hazard to occupational workers, methods for its efficient removal, sensitive techniques to analyze for its presence, etc., need to be raised and addressed. Currently, we are unaware of definitive work which has identified and quantified S_2F_{10} in actual utility samples. Indeed, investigations for the presence of S_2F_{10} in such samples must rely on sophisticated analytical techniques, since the analytical requirement is to detect and quantify low (to very low) concentrations of a particular molecular species in an abundant milieu of a very similar molecular species (SF_6). Nevertheless, studies from a few laboratories have produced evidence that S_2F_{10} may be produced and accumulate as a result of electrical discharge in SF_6, under certain conditions and experimental designs. Thus, Pettinga (1985) demonstrated the presence of S_2F_{10} at very low concentrations (50-100 ppb) following a power arc burnthrough experiment. Work in the laboratory of I. Sauers has demonstrated that: (1) electric spark decomposition of SF_6 in a spark chamber can produce S_2F_{10} ($4\text{-}37 \times 10^{-11}$ mol/J) (Sauers et al., 1988a; 1988b; 1990); and (2) corona decomposition of SF_6 can produce highly significant yields of S_2F_{10} (2-15 μmoles/Coulomb) (Sauers et al. 1989; 1990; Olthoff et al. 1990a).

PHYSICAL/CHEMICAL PROPERTIES OF S_2F_{10}.

It is not the purpose of this discussion to provide an extensive overview of the physico-chemical properties of S_2F_{10}. Nevertheless, a few properties relevant to subsequent discussion will be mentioned. S_2F_{10} has a melting point of -53° C, and boils at 30.1° C (Renshaw and Gates, 1946;

Eibeck and Mears, 1980). Its vapor pressure at 25° C is 675 mm Hg (Renshaw and Gates, 1946). It is quite insoluble in water, but soluble in a variety of organic solvents (e.g., acetone) (Cotton and Wilkinson, 1980; Renshaw and Gates, 1946). The compound can be decomposed by heating; below 200° C this decomposition is very slow, but proceeds rapidly at higher temperatures (Benson and Bott, 1969). S_2F_{10} does not react with common laboratory strong alkalis or acids. Activated charcoal catalytically decomposes S_2F_{10} (the stated products of this decomposition are SF_6 and SF_4) (Renshaw and Gates, 1946). In the S_2F_{10} molecule, each S is octahedral, and surrounded by 5 fluorines. While the individual S-F bonds are shorter by about 0.2Å than expected (thus stronger than anticipated for an S-F single bond), the S-S bond is unusually long (2.21Å as compared to 2.08Å expected for S-S) (Cotton and Wilkinson, 1980). The weakest bond in the S_2F_{10} molecule is thus apparently the S-S bond, and its breaking accounts for the decomposition products produced by heating or charcoal catalysis. S_2F_{10} is stated to be an oxidizing agent (Renshaw and Gates, 1946). Presumably, the chemistry underlying this assertion must involve the S-S bond.

ANIMAL TOXICOLOGY

One of the most interesting (and potentially important) properties of S_2F_{10} is its strong toxicological action. Apparently this particular property was recognized rather early after its discovery (in 1934 by Denbigh and Whytlaw-Gray) as it was considered as a candidate chemical warfare agent for use in World War II (see Renshaw and Gates, 1946). A further feature making S_2F_{10} attractive for military application was its insidious nature, as it provided little warning of exposure. (It did not produce lacrimation or skin irritation at toxicologically significant concentrations.) Pure samples are stated to be odorless and non-irritating to the respiratory tract, at least following brief exposures to concentrations up to 0.2 mg/L of air (Renshaw and Gates, 1946). On the other hand, some individuals have described an odor similar to SO_2 upon exposure to commercial preparations of S_2F_{10} (Renshaw and Gates, 1946). Whether these samples contained small contaminating concentrations of other sulfur-containing compounds was not determined.

The study of S_2F_{10} as a candidate warfare agent resulted in animal toxicology evaluations, and these data provide the most extensive extant source for the whole-animal toxicity of this compound. In Table 1 these toxicity data are considerably condensed from the data presented in the National Defense Research Committee (NDRC) report (Renshaw and Gates, 1946). We present only the LC_{50}'s for 1 and 10 min. exposures, although 30 min exposure times were also tested. It was found that the LCt_{50} (i.e., air concentration of S_2F_{10} x time of exposure, which produced lethality in 50% of the animals so exposed) did not significantly vary over the range of 10-30 min. This suggests significant detoxification over these short times of exposure was not occurring. Although the data in Table 1 do not provide evidence of this feature, the NDRC report indicates that there was a narrow range of S_2F_{10} concentration between that causing no death and that producing 100% mortality. The species differences in sensitivity to S_2F_{10} toxicity do not appear to be very marked, except in the case of the rhesus monkey. Animals exposed to lethal doses gave no indication during the course of exposure of impaired respiration or respiratory irritation. The majority of the animals died in the time period between 3 and 20 h after exposure. The initial symptoms were respiratory distress, which progressed to convulsions and death. The pathology seen in animals exposed to S_2F_{10} was consistent with classifying it as a pulmonary irritant. Death resulted from anoxia (lack of oxygen) due to a vigorous pulmonary edema (lungs filled with fluid) and hyperemia (blood in the lungs). Interestingly, no effects on other tissues attributable directly to S_2F_{10} were seen.

The purpose of these military toxicology studies was to evaluate S_2F_{10} as a chemical warfare agent. On the basis of the results observed, S_2F_{10} was considered to be <u>possibly</u> as toxic as phosgene. For some animal species, S_2F_{10} demonstrated a stronger acute toxicity than phosgene. In the case

of the monkey, however, S_2F_{10} was only ~1/10 as toxic as phosgene. If the monkey is considered to be the best animal model for humans, then S_2F_{10} may be significantly less toxic than phosgene. Such an evaluation is very tentative, considering the limited data and the lack of understanding of the basic mechanism of S_2F_{10} toxicity.

Greenberg and Lester (1950) carried out S_2F_{10} toxicity studies in the rat which apparently form much of the basis for the setting of the Threshold Limit Value (TLV) proposed by the American Conference of Governmental Industrial Hygienists (ACGIH) for S_2F_{10}. The purity of the S_2F_{10} used in this study was not stated; the supplier was Allied Chemical Co. Exposures to 5% S_2F_{10} concentrations resulted in animal death within a few minutes. Exposure to 1780 ppm produced death at 1 h of exposure. Groups of animals (very small groups) were then exposed to various low concentrations of S_2F_{10}, and animals were autopsied immediately following exposure termination or 24 h later (see Table 1). Exposure to 10 ppm or 1 ppm for 1 h produced lung lesions in rats as detected immediately after exposure, although after 24 h recovery, no lung pathology was seen. Longer exposure times (18 h) were then tested. Of six rats exposed to 1 ppm all died within 16 h, and autopsy revealed extensive lung damage (edema and lung hemorrhages). Animals exposed to 0.5 ppm or 0.1 ppm survived the 18 h exposure, but autopsies immediately following the exposure termination showed significant lung damage from 0.5 ppm S_2F_{10} and a generalized lung irritation (i.e., generalized pinkness in the lungs) from 0.1 ppm. These authors confirm the NDRC observations that S_2F_{10} did not produce eye or nose irritation in any of their animal groups, and therefore they also emphasize the insidious nature of the S_2F_{10} hazard. They concluded that human exposure to S_2F_{10} should not exceed 0.01 ppm (10 ppb).

The accuracy with which these authors were able to prepare these very low concentrations of S_2F_{10} could not be determined, nor is any indication given of attempts to analyze the S_2F_{10} concentrations in the exposure chamber air. In the supporting documentation for the ACGIH establishment of the 10 ppb ceiling TLV for S_2F_{10} (ACGIH, 1986), the Greenberg and Lester study is cited along with only one other study, a report of work by Saunders et al. (1953). In the Saunders study, the S_2F_{10} was dissolved in a lecithin-saline emulsion and administered intravenously. We do not find this study to be particularly relevant to possible exposures to degraded SF_6 gas. Finally, we are aware of only one other study relevant to animal toxicity of S_2F_{10}, which appeared in abstract form in 1980 (see Table 1, work of O'Neill et al.). There is insufficient information provided to evaluate the purity of the S_2F_{10} gas used, the accuracy of the dilutions prepared, etc. The authors again remark on the insidious nature of S_2F_{10}, and note that over a time period of exposure up to 18 h, the toxicity appears to be proportional to the product of S_2F_{10} concentration x time of exposure.

OUR EXPERIENCE WITH BIOLOGICAL PROPERTIES OF S_2F_{10}: IN VITRO CELL CULTURE STUDIES

Over the past 4 years, we have carried out extensive investigations of the toxic action of S_2F_{10} using a cell culture system. S_2F_{10} mixtures in SF_6 have been made and analyzed by gas chromatography, and concentrations of S_2F_{10} from 5-5000 ppm have been tested against 3 separate cell lines. These data have been reported in detail elsewhere (Griffin et al., 1989a; 1989b; 1990) and will be only briefly summarized here. We find S_2F_{10} to be literally orders of magnitude more toxic than other SF_6 breakdown products (e.g., SOF_2, SO_2F_2, SOF_4, SiF_4, HF, etc.) in our cell culture systems (Fig. 1A). We find that the slope of the S_2F_{10} cytotoxicity vs. concentration curve is very steep (much more so than any other breakdown product we have tested), so small changes in S_2F_{10} concentration produce large changes in cytotoxic effect (Fig. 1B). This further means that the difference in S_2F_{10} concentration between no effect and 100% cell killing is small. Note that this same phenomenon was also observed in whole-animal studies (Renshaw and Gates, 1946). We have

observed that the S_2F_{10} content of spark-decomposed SF_6 samples accounts for essentially all the cytoxic effect produced by these samples, and that destruction of the S_2F_{10} content by heating essentially eliminates the cytotoxicity of these sparked SF_6 samples. The different cell lines we use do show a somewhat different sensitivity to S_2F_{10}, although the sensitivity does not vary dramatically. We also find that the length of time of exposure is critical in determining S_2F_{10} cytotoxicity, and we have confirmed the previously cited results from animal studies, i.e., that the toxicity of S_2F_{10} can be expressed as a product of concentration and time. (Longer exposures to lower concentrations are equivalent to shorter exposures to higher concentrations.) To illustrate this, consider the following cytotoxicity data for one cell line CHO = (Chinese Hamster Ovary). Based on concentration vs. response curves for 1 h of exposure, the concentration of S_2F_{10} that kills 99% of the cells is 600 ppm. The LCt_{99} is therefore 600 ppm-h. Exposure of the cells for 24 h to 25 ppm produces $\geq$ 99% cell killing. Thus, the LCt_{99} for these particular conditions is also 600 ppm-h. It appears that the cytotoxic response is directly related to time of exposure, at least over the range of 1-24 h. The minimum concentration of S_2F_{10} which has shown cytotoxicity in our system is 25 ppm (24 h of exposure). This is a considerably higher concentration than was found to be minimally effective in producing toxicity in the whole animal (e.g., 0.1-1 ppm in the work of Greenberg and Lester). There are, of course, many differences between whole animal and in vitro systems. Nevertheless, we think that we can substantially increase the sensitivity of our cell culture system to the cytotoxic activity of S_2F_{10}. It is virtually certain that a degree of protection from the lethal effects of S_2F_{10} is afforded to our cells by: (1) being bathed (albeit periodically) in aqueous tissue culture medium; and (2) being bathed in fluid containing animal serum. Remember that: (1) S_2F_{10} is very insoluble in aqueous solution; the gas may therefore not be able to penetrate the thin liquid film overlying the cells. Simply slowing the rotation of the tubes in the roller drum in our exposure system may provide more effective exposure; and (2) animal serum has been shown to have significant protective effects for cells exposed to a variety of agents (e.g., Rasmussen, 1984). It would be a simple matter for us to carry out our exposures in serum-free conditions.

EVALUATION OF DECOMPOSITION PRODUCT REMOVAL METHODS

The use of absorbers/scrubbers to remove corrosive and toxic decomposition products of SF_6 has been considered for at least 40 years. It was realized early on that toxic species such as SOF_2 should be removed to prevent possible exposure to maintenance workers. Also, such products as HF needed to be eliminated due not only to its toxicity but also to its highly corrosive effect on insulator materials and metals. Absorbers are now installed directly in some equipment and are used in gas reclaimer carts and separate filter/purifiers. A review of the literature concerning absorber studies appears in the EPRI Report EL-1646 (Baker et al., 1980).

A number of studies have indicated that the best materials for removal of decomposition products such as SOF_2, SO_2F_2, and SO_2 are activated alumina (porous Al_2O_3), soda lime (NaOH + CaO), and molecular sieve material (zeolite, containing Al_2O_3, SiO_2, and an alkali metal such as Na). These materials also act to absorb moisture. Activated charcoal has also been studied as an absorber (Baker et al., 1980). Commercial gas carts have internal purification cartridges to clean up SF_6 when it is being removed while equipment is serviced. For cases in which SF_6 is badly decomposed, separate purifiers have been developed to provide additional cleanup capacity. (Commerical devices are manufactured by companies such as LIMCO Manufacturing Corp., Glen Cove, NY and Cryoquip Corp. Murrieta, CA). As an example, one such system (LIMCO Series 2000 Rechargeable SF_6 Gas Filter-Purifier) contains four chemical beds separated by diffuser plates which remove different species, including one each for HF, moisture, oil vapors, and sulfur fluoride compounds. In addition, particle filters remove solid products down to 2 microns in size. The LIMCO filter and an experimental one assembled by Allied Chemical Co. were tested for their ability

to filter out decomposition products from a 13.1 kA arc between Al electrodes with a duration of four cycles (Baker et al., 1980). The Allied unit contained soda lime, activated alumina, and a molecular sieve. The amounts of SOF_2 and SO_2F_2 present after flowing the gas through the scrubbers were each less than 100 ppm which was the detection limit of the analysis. In their product literature, LIMCO claims that their system can achieve a final concentration for those two species of 10 ppm by volume. It should be noted that in the EPRI study S_2F_{10} was not detected in arced samples or reference samples. This could be due to the use of Poropak Q column which has recently been shown by Olthoff et al. (1990a) to be unable to separate S_2F_{10} from SF_6. Hence, it is not known how effective these type of absorber materials are for S_2F_{10}. It is unlikely aqueous alkali (soda lime) alone would be very effective in absorbing/reacting with S_2F_{10}, due to its lack of solubility in aqueous solution. The studies relating to its use as a warfare agent indicate activated charcoal was a suitable agent for decomposing S_2F_{10}. If this decomposition is related to a surface catalysis effect [work from the laboratories of I. Sauers and R. Van Brunt suggests a generalized phenomenon of decomposition of S_2F_{10} on, at least, metallic surfaces (Olthoff et al., 1990b)], then other materials such as alumina may be as effective. Determination of the efficacy of various scrubber materials for S_2F_{10} awaits further research.

CONCLUDING COMMENTS

Whether S_2F_{10} does, in fact, exist to a significant degree in electrically-stressed SF_6 in utility settings is a question still to be answered. The underlying mechanisms by which this compound produces its toxic effects and the reasons it should be much more toxic than compounds of similar structure (i.e., SF_4) remain to be elucidated. Indeed, we have obtained preliminary evidence that $S_2F_{10}O$ shows no cytotoxicity in our cell culture system, even when tested at concentrations up to 5,000 ppm. Thus, the particular molecular structure of S_2F_{10} must be determinative in regard to its toxicity. Also, a better understanding of the chemistry of S_2F_{10} might serve to suggest appropriate amelioration techniques. Finally, understanding the molecular basis of the physiological/biochemical effects of S_2F_{10} may have applicability extending beyond the relatively narrow and focused interest in this particular toxic agent. The knowledge gained from such studies may open doors to other heretofore obscure or misunderstood areas of toxicology.

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Table 1. Animal Toxicity of S_2F_{10}

A. Renshaw and Gates, 1946

Species	Exposure Time (min)	LC_{50} (ppm)[1]
Mouse	1	133-209
	10	9.5-19
Rat	1	218
	10	19-28
Guinea Pig	10	38-57
Rabbit	10	38-57
Monkey	10	86

B. Greenberg and Lester, 1950 (Rats)

S_2F_{10} Concentration	Exposure Time (h)	Toxic Effect
10 ppm	1	hemorrhages in lung
1 ppm	1	severe lung congestion
0.1 ppm	1	no effect
1 ppm	16	lethal lung hemorrhages
0.5 ppm	18	severe lung lesions
0.1 ppm	18	lung irritation
0.01 ppm	18	no effect

C. O'Neill et al., 1980

Species	LCt_{50} (ppm x min)[2]
Mouse	120
Rat	127
Guinea Pig	412

[1] LC_{50} = concentration of a substance in air which causes death of 50% of animals exposed for the indicated period.

[2] LCt_{50} = concentration of a substance in air times duration of exposure, the product causing 50% mortality.

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Fig. 1A. Comparative cytotoxicity of various SF_6 decomposition products

Fig. 1B. Change in cytotoxic effect as a function of unit change in gas concentration for various SF_6 decomposition products

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