EVALUATION OF POSSIBLE BIOLOGICAL EFFECTS FROM EXPOSURE TO GASEOUS SF_6 BREAKDOWN PRODUCTS

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Abstract

A variety of chemical byproducts (e.g., SOF_2, SO_2F_2, SF_4, HF, SO_2, etc.) are produced at varying concentrations by electrical arcs, sparks or corona discharge in SF_6; most of the byproducts are toxic to some degree. Using a cell culture system, we have studied the toxicity of individual byproduct gases, as well as electrically decomposed SF_6. The toxic potency of various byproducts can be compared, using this cellular assay. The animal toxicological data for these gases, although sparse, is also reviewed. The rationale for selection of various byproduct gases as monitors for evaluating the hazard potential of decomposed SF_6 is discussed.

1. Introduction

Sulfur hexafluoride (SF_6) has excellent electrical insulating properties and is widely employed in electrical applications, including gas-insulated substations and switchgear. Although SF_6 itself is devoid of toxic effects (except that at high enough concentrations it is an asphyxiant), concerns arise regarding some of the byproduct gases which may be present following electrical discharges in SF_6. Depending upon conditions (the nature of the discharge, presence of water, vacuum greases, etc.), a wide variety of product gases, such as SOF_2, SO_2F_2, SF_4, SOF_4, SO_2, HF, S_2F_{10}, S_2OF_{10}, etc. may be present in varying amounts, along with metal fluorides and other secondary products like SiF_4 /1/,/2/. Exposures of animals to electrically decomposed SF_6 has demonstrated it can produce acute toxic effects /3/. Inadvertent exposures (in which good industrial hygiene practices were not followed) to decomposed SF_6 have also resulted in human toxicity /4/. Evaluation of the hazard potential of decomposed SF_6 requires knowledge of the quantities of the various byproducts present, and knowledge of their toxicities. Rational selection of which byproduct gases to use as monitors for evaluating extent of decomposition and potential toxicity of SF_6 from various conditions also depends upon knowledge of byproducts and their biological activity. In this paper, the toxicity of some of the more common/abundant gaseous byproducts of SF_6 will be discussed; animal toxicity, where known, will be reviewed, as well as results from this laboratory's cell culture studies.

2. Gaseous Decomposition Products of SF_6

Listings of various byproducts found in decomposed SF_6 samples have been published by us and others /1/,/2/; the following is not intended to be encyclopedic, but to cover the range of more commonly encountered species. Table 1 provides a listing of some of the byproduct species found in laboratory samples of spark-decomposed SF_6 gas, along with quantities present under a given set of spark conditions. Spark and arc discharges in SF_6 decompose the gas into atoms of S and F, which subsequently recombine to form SF_6 (mainly), SF_4 and SF_5 · radical (combination of 2 SF_5 · radicals yielding S_2F_{10}). SF_4, which is the major byproduct of SF_6 decomposition, rapidly hydrolyzes to SOF_2 and HF if water vapor is present. SOF_2 is usually considered to be the main stable product of SF_6 decomposition. The sulfoxyfluorides, SOF_4 and SO_2F_2, form from the reaction of atomic oxygen with the primary SF_6 breakdown products. Further hydrolytic reactions of various products form additional HF as well as SO_2. HF can react with ceramic insulators to form SiF_4. S_2OF_{10} and $S_2O_2F_{10}$ have recently (unpublished data) been identified and quantified in various laboratory-produced samples by one of us (I. Sauers). Based on recent preliminary data, the yield of $S_2O_2F_{10}$ was greater than that of S_2F_{10} under the same conditions (Table 1, footnote d). These products and their concentrations do not necessarily mirror the composition of decomposed SF_6 samples from field equipment, but provide a frame of reference for further discussion. Recent analyses of arced SF_6 samples have shown that many of the same products can be found in such samples (including S_2F_{10}) although concentrations may vary widely /5/.

3. Review of Animal Toxicity

The biological database for many of the SF_6 decomposition products is very sparse or altogether lacking. Table 2 provides a somewhat selective summary of the animal toxicity data which we have identified. Only LC50 values (defined in Table 2) are included, although for a number of the gases LCLo (lowest concentration of a gas in air, other than the LC50, which has been reported to have caused death in animals) values were available. A decision was made not to include LCLo values because these values reflect many uncontrolled (perhaps uncontrollable) variables, and as such represent toxicological "snapshots" of a given animal's susceptibility under a unique experimental protocol, rather than a dose-response study arranged over a reasonable animal population (such as an LC50 study). The LC50 values

Table 1: Decomposition Products Found Following Repeated Sparking in SF_6

Product	Approximate Concentration in Sparked SF_6 [a]
SOF_2 (SF_4) [b]	0.5%
SOF_4	0.085%
SiF_4	0.026%
S_2F_{10}	0.026% [c] (0.031%) [d]
SO_2F_2	0.006%
SO_2	0.002%
HF	1.0% [e]
S_2OF_{10}	0.0013% [d]
$S_2O_2F_{10}$	0.445% [d]

a 16 kJ total energy deposited in 70 cm^3 gas volume at 133 kPa total pressure. Concentrations taken from Ref. 12.

b SF_4 quickly hydrolyzes to SOF_2. The indicated concentration reflects SF_4 production immediately after sparking or SOF_2 after several minutes following sparking.

c Yield of S_2F_{10} depends strongly on moisture in the system, falling in the range 0.04-0.37 nmol/J. The value given here arises from sparks produced under very dry conditions /13,/14/.

d S_2F_{10}, S_2OF_{10}, and $S_2O_2F_{10}$ were recently measured in a 1.1-l spark cell for total energy E < 300 J. Concentrations have been normalized to 16 kJ deposited in a 70 cm^3 gas volume.

e Concentration was not measured but was calculated based on SF_4 hydrolysis which leads to its production. The amount should be considered an upper limit, since HF may be lost to secondary reactions or to chamber walls.

(with the exception of the value for SiF_4) were extracted from the latest version of the Registry of Toxic Effects of Chemical Substances /6/,/7/. Some idea of the relative toxicity of various gases can be obtained by comparison of LC50 values. Since exposure times vary widely, the assumption has been made that total inhaled dose = concentration of gas in air (ppm) x time of exposure. Thus for the single species (rat) for which LC50 data for more than two compounds in Table 2 is available, a relative toxicity ranking (from least toxic to most) would be: $SO_2F_2 < SO_2 < HF \leq SiF_4 << S_2F_{10}$.

Threshold Limit Values (TLVs) are also listed in Table 2, and are guidelines for good industrial hygiene practice established by the American Conference of Governmental Industrial Hygienists (ACGIH)/8/. ACGIH documentation cautions that these TLVs are "not fine lines between safe and dangerous concentrations, nor are they a relative index of toxicity"/8/. As an example, note that SO_2 has a lower TLV than HF, while the LC50 values suggest that HF is a more acutely lethal hazard than SO_2. For two of these gases, SOF_2 and SiF_4, TLVs are based on the recommended value for inorganic fluorides [2.5 mg(F)/m^3], and ppm TLVs have been calculated as indicated. As can be seen in Table 2, toxicity data for a number of gases of interest is very fragmentary. Since SOF_2 is one of the most

Table 2. Acute Animal Toxicity and Threshold Limit Values for Various SF_6 Decomposition Products

Compound	LC50 [a]	TLV [b]
SOF_2	--- [c]	1.6 [d] ppm
SO_2F_2	991 ppm/4h [e]	5 ppm
SF_4	----	0.1 ppm [f]
SOF_4	----	----
SiF_4	922 ppm/1 h [e]	0.8 ppm [d]
S_2F_{10}	193 ppm/10 min [e] 96 ppm/10 min [g] 386 ppm/10 min [h,i] 868 ppm/10 min [j]	10 ppb [f]
S_2OF_{10}	----	----
$S_2O_2F_{10}$	----	----
SO_2	2520 ppm/1 h [e] 3000 ppm/30 min [g]	2 ppm
HF	342 ppm/1 h [g] 1276 ppm/1 h [e] 1774 ppm/1 h [j] 4327 ppm/15 min [i]	3 ppm [d,f]

ppm = parts in 10^6; ppb = parts in 10^9

a. LC50 = a calculated concentration of a substance in air, exposure to which for a specified time, is expected to cause death of 50% of a defined animal population. (Values shown are concentration for a given exposure time).

b. TLV (TWA) = threshold limit value (time-weighted average) = the time-weighted average concentration for a normal 8 h work day or 40 h work week, to which nearly all workers may be repeatedly exposed without adverse effect

c. No information available

d. Generally recommended TLV value for inorganic fluorides = 2.5 mg (F)/m^3, from which ppm TLV was calculated, applying the following formula TLV (ppm) = $\frac{\text{TLV (mg/m}^3\text{) x 24.45}}{\text{atomic weight F (grams)}}$

e. Test animal = rat

f. Ceiling Limit = concentration which should not be exceeded, during any part of the work day. If instantaneous monitoring is not feasible, then ceiling should be assessed as a 15-min time-weighted average exposure

g. Test animal = mouse

h. Test animal = rabbit

i. Test animal = guinea pig

j. Test animal = monkey

abundant byproducts usually detected, it was deemed important to present any animal toxicity information available for this gas. The work of Truhaut et al /9/ provides some data, although the number of animals are small, and dosage ranges are not conducive to studying dose-response relationships. For 1 h exposure of rats, 0/5 (0 out of 5) male rats died within 24 h of exposure to 150 ppm of SOF_2, while 10/10 died with 200 ppm of SOF_2. For male mice, 1 h exposures to SOF_2 produced 0/10 deaths at 260 ppm, while 10/10 died at 300 ppm. Truhaut et al /9/ state that autopsies and microscopic examination of tissues from animals surviving the exposures indicated lung damage (presumably for even the lowest concentrations tested). Thus a no-effect dose for SOF_2 could not be established from this study, but would certainly be lower than 100 ppm (1 h exposure). LCLo values for SF_4 and S_2OF_{10} (19 ppm/4 h and 20 ppm/6 h, respectively) were listed in the Toxic Effects Registry /6/, but time of exposure is very different for these gases in comparison to SOF_2. It should be stressed that establishment of values at which no biological damage is seen are probably much more valuable than LCLo values for evaluating relative toxicity and such values could not be derived for most gases of interest.

4. Cellular Toxicity Studies

In vitro cell culture studies of toxicity cannot be directly extrapolated to either human or animal toxicity (the extrapolation from animal to human is also fraught with difficulty), but can provide useful information for relative rankings of toxicity. Because of the relative lack of animal toxicology information regarding gaseous SF_6 decomposition products, our research efforts have been directed to carrying out cell culture toxicity assays to determine dose-response relationships for the individual gases. The experimental details of this biological assay have been published extensively before /10/,/11/, and will not be repeated here. Cells in culture are exposed directly to the gas of interest (using a novel exposure system developed in this laboratory) for 1 or 4 h, and subsequently assayed for the percentage of remaining viable cells, using reproductive viability as the criterion. This reproductive cell survival assay is well-established as a measure of in vitro toxicity, and has been used for both chemicals and agents like ionizing radiation. All cell survival results are expressed as relative cell survival, i.e., survival of test gas-exposed cells compared to survival of cells exposed to SF_6.

Results of these toxicity studies for the gases S_2F_{10}, SO_2F_2, SOF_2, SOF_4, and SiF_4 are shown in Fig. 1 for 4 h exposures. The toxicity curve for SF_4 was found to track almost exactly the curve shown for SOF_2, which is expected as SF_4 would certainly hydrolyze to SOF_2 very rapidly in the aqueous environment of our cell culture assay system. The toxicity curve for SOF_4 similarly tracks very closely the curve for SO_2F_2, but is displaced to the right [midpoint of SOF_4 curve (50% cell killing) is at 8000 ppm, compared to 3300 ppm, the midpoint for the SO_2F_2 curve]. Again, this is to be expected, from the hydrolysis of SOF_4 to SO_2F_2. Comparisons of the toxicity curves in Fig. 1 for the various gases indicates that there are large differences in the cytotoxic (cell killing) effect of the different gases. S_2F_{10} produces strong cellular lethality in the 100 ppm range, while SO_2F_2 produces similar levels of lethality in the 1000s of ppm range. SOF_2 and SiF_4 show cell killing activity in the 10,000s of ppm range. In Fig. 1 the slopes of the cytotoxicity curves for the various gases appear to be very similar, but this appearance is somewhat misleading, because of the log scale on the abscissa. Thus S_2F_{10} has a gradation from 0% cytotoxicity to 100% cell killing over a range of ~300ppm, while SOF_2 has a similar change in biological response over a concentration range of 45,000 ppm. It can be seen that S_2F_{10} shows changes in toxic effect over much narrower concentration ranges than any of the other gases (in fact, there is a ~50-fold difference between S_2F_{10} and the next most toxic gas). Therefore, even though S_2F_{10} may be present in decomposed SF_6 at much lower levels than other byproducts, relatively small changes in its concentration may produce large changes in its contribution to overall cell killing potency of the gas mixture. In fact, in our cell culture system, S_2F_{10} may play a dominant role in determining the toxicity of sparked SF_6 samples, even though other byproducts (like SOF_2) are present in much larger absolute amounts. However, for other types of discharges, the situation may be different as discussed below.

5. Evaluation of Relative Toxicity Data

Evaluation of the toxicity of a complex mixture of toxic agents is a difficult undertaking, and depends upon many factors, perhaps the most important being the concentration of individual agents, and the overall dose-response characteristics of each individual agent. As an illustration, consider comparison of toxicity of S_2F_{10} and SOF_2 in cell cultures, using 50% cell lethality as the common toxicity endpoint. For the S_2F_{10} - SOF_2 pair in our cell culture assay, the relative toxicity of S_2F_{10} vs. SOF_2 at 50% cell lethality is ~180. It is interesting to note that the ratios of the TLVs for S_2F_{10} and SOF_2 are ~160. However, since TLVs are not, in general, intended to be used for ranking relative toxicity, there is no guarantee that there will be a good correspondence between TLVs and cellular lethality and/or LC50 data.

If one wishes to use one of the SF_6 byproducts as a toxicity "surrogate" for the overall complex mixture, then a logical choice for such a "surrogate" would be a component which was present in reasonable concentration (not a trace component), and also displayed a reasonably strong toxicity. SOF_2, at first glance, seems to be such a "surrogate" as it is one of the most abundant species in decomposed SF_6, and it is quite toxic. If SOF_2 is therefore used as the surrogate for the total mixture, then will control of SOF_2 to below its TLV ensure that other individual toxic components will also be controlled to below their TLVs? If the SOF_2 concentration in a particular sample is 1000 ppm, and S_2F_{10} is 10 ppm, then a decrease in SOF_2 concentration to 1 ppm (~TLV) will result in a corresponding decrease in S_2F_{10} to .01 ppm (its TLV). (This assumes that the method for decreasing concentrations affects both species in the same proportion.) If, on the other hand, the SOF_2 concentration is 100 ppm and the S_2F_{10} concentration is 10 ppm, then reducing SOF_2 100-fold will only reduce S_2F_{10} to 0.1 ppm, 10-fold above the TLV. Thus the relative concentrations of the two agents in any given mixture will determine whether control of one to its TLV will also reduce the other to its TLV. For the example of laboratory spark samples in Table 1, reducing SOF_2 to its TLV does not reduce S_2F_{10} to its TLV. For power arcs, control of SOF_2 to its TLV may well provide control of all other components since the SOF_2 yield increases significantly over the yield in spark discharges /1/. Establishment of expected concentrations of the various toxic byproducts under a variety of fault conditions is thus essential to predicting whether control of all species to their TLVs is feasible by controlling one abundant component to its TLV. One of the objectives of a Co-operative Research & Development Agreement, of which Oak Ridge National Laboratory is a part, is a field survey of SF_6 equipment at Ontario Hydro and other participating utilities, to provide information on byproduct concentrations in actual equipment.

6. Conclusions

A number of gaseous decomposition byproducts of SF_6 can be produced upon electrical discharge in the gas and their concentrations can vary widely, depending on conditions. Many of these byproducts are very toxic, both

in animals and cell culture assay systems. Relative toxicity comparisons from animal data are difficult due to scarcity of data. Cell culture studies in our laboratories have allowed us to make relative comparisons of cell killing efficiency for a number of the products. S_2F_{10} is much more toxic to cells than other products, followed by (decreasing toxicity) SO_2F_2, SOF_2 and SiF_4. Control to TLV levels of an abundant byproduct may or may not insure control of other byproducts to their TLVs, depending on relative concentrations in the gas mixture. Further research regarding relative abundance and toxicity characteristics is called for.

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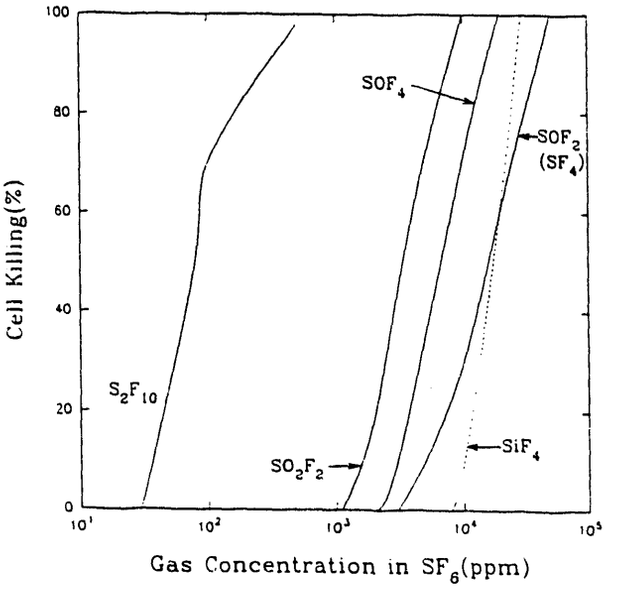

Fig. 1 Concentration vs. Cellular Lethality of Various SF_6 Byproducts, 4h exposure times, gases diluted in SF_6 to indicated concentrations. Dose-response curves fit by computer to data points (not shown).

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