THE DEVELOPMENT OF A NOVEL CATALYTIC TECHNOLOGY FOR CF_3I MANUFACTURE

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INTRODUCTION

F-TECH INC., (previously known as **JAPAN** HALON) was established in 1975 to produce Halon 1301 and Halon 1211. Ownership was held 50/50 between Toyo Soda Manufacturing Corporation (now Tosoh Corporation), and Onoda Cement Corporation (now Taiheiyo Cement Corporation).

Our patented halon technologies were proprietary and unique, namely, continuous vapor fluorination and bromination reactions. Following the Montreal Protocol, F-TECH management decided on a phase-out of its halon manufacture and embarked upon intensive R&D efforts to develop other kinds of fluorochemicals, including halon alternatives. Our emphasis was centered upon compounds that would offer low ODP and low or minimal global warming potential. This program started in 1993 and has continued to the present time.

Over the past several years, our researchers focused much effort on the development of a continuous vapor phase process for the manufacture of CF_3I, which was reported to be a leading Halon 1301 alternative for use in unoccupied areas. **EPA's** continuing interest in CF_3I has encouraged our company to refine its proprietary CF_3I technology and the purpose of my presentation today is to acquaint all interested parties with F-TECH's progress and its plan for CF_3I commercialization.

Basically, our technology relies on a novel catalytic method that takes full advantage of F-TECH's experience in vapor phase halogen chemistry.

$$CHF_3 \quad + \quad I_2 \xrightarrow{\text{Cat.}} CF_3I \qquad \text{(Reaction 1)}$$

In our process, it is possible to readily produce CF_3I by reacting CHF_3 with I_2 in the presence of a unique catalyst system (Scheme-I). Other technologies are also reported in the literature such as the reaction of the metal salts of trifluoroacetic acid and iodine (Scheme-2) [1, 2]. Recently, another process involving the electrochemical reaction of bromotrifluoromethane (CF_3Br) with zinc followed by the addition of chloroiodine (Scheme-3) [3] was reported. These reported technologies would not seem likely candidates for large tonnage CF_3I scale-up due to low yield, disposal of byproduct ZnBrCl, and the fact that they are hatch processes.

The authors of this paper are grateful to the sponsors of this conference for the opportunity to present more insight into F-TECH's novel CF_3I technology.

$$CF_3CO_2M \quad + \quad I_2 \xrightarrow{-CO_2} CF_3I \quad + \quad MI \qquad \text{(Reaction 2)}$$

M : Na, K, **Ag** etc.

$$CF_3Br + Zn \xrightarrow{e^-} (CF_3ZnBr) \xrightarrow{ICl} CF_3I + ZnBrCl \qquad \text{(Reaction 3)}$$

EXPERIMENTAL

The catalyst was prepared by common impregnated methods such as the following. Activated carbon was added to the solution including various aqueous metal salts and then dried under pressure. This pre-catalyst was calcined under nitrogen stream at 400-550 °C. At this point the catalyst was charged to a Hastelloy C reactor. heated to reaction temperature, and mixed CHF_3 and I_2 gases were added. Following completion. reaction gases were cooled to condense unreacted iodine in the vessel. After separating unreacted iodine, the reaction gases were washed, dried, and trapped in the cooled cylinder. The products were then analyzed by both of GC and GC analyses.

RESULTS AND DISCUSSION

THE SCREENING OF CATALYST COMPONENT

Many kinds of catalysts were tested in this reaction. The tested catalysts are made from a kind **of** alkali metal salts or of alkaline earth metal salts and activated carbon as **a** carrier. Our reseachers found that the alkali metal salts selected showed a higher catalytic activity than the alkaline earth metal salts. Table I presents a comparison of the alkali metal salts that were screened in our work. The order *of* activity in the catalysts involving alkali metals is Rb, Cs > **K** > Na and the order of selectivity is K > Rb, Cs > Na (Table I). Based on exhaustive studies, it was found that the most suitable catalyst for this reaction is the synergistic combination of K^+ having high selectivity and Rb^+ or Cs^+ of high activity. In contrast, the anion, countcr-ion, to the metal salts has no observable effect on the reaction mechanism or rate. After reaction, counter-ion included all kinds of used catalyst were changed to fluoride ion by hydrogen fluoride of a byproduct.

CATALYST CARRIER SCREENING

Numerous kinds of catalyst carriers were evaluated in our bench trials, including SiO_2, Al_2O_3, SiO_2-Al_2O_3, TiO_2, ZrO_2, AC. Graphite, ACF, and others. The results show that the catalyst using a carbonaceous carrier only had catalytic activity, and it was dependent on the surface area of carrier (Table 2). The other carrier does not have catalytic activity. and it decomposed under the reaction conditions.

THE ANALYSIS OF PRODUCTS

The following products were detected by both of GC and GC-Mass analyses (Table *3)*. The main products are CF_3I, CF_4, C_2F_5I, and smaller amounts of perfluoroalkane derivatives like C_3F_8. The product distribution suggests that the reaction mechanism is proceeding through a CF_2 carbene intermediate. Based on the isolated products, Scheme-4 is indicative of a stoichiometric reaction equation. It clearly shows that a disproportionate process is involved in this reaction.

TABLE 1. CATALYST EFFECT COMPARISON.

Component	CHF_3 Conv.(%)	CF_3I Sel.(%)	Component	CHF_3 Conv.(%)	CF_3I Sel.(%)
$NaNO_3$	16	0	KCI	63	62
KNO_3	68	53	KF	13	47
$RbNO_3$	83	38	KOH	65	54
$CsNO_3$	84	22.5	KOAc	62	54

TABLE 2. RELATIONSHIP BETWEEN SURFACE AREA AND ACTIVITY.

Carrier	Surface Area (m^2/g)	CHF_3 Conv. (%)	CF_3I Sel. (%)
A	1000-1200	34.9	65.1
B	510	15.1	60.8

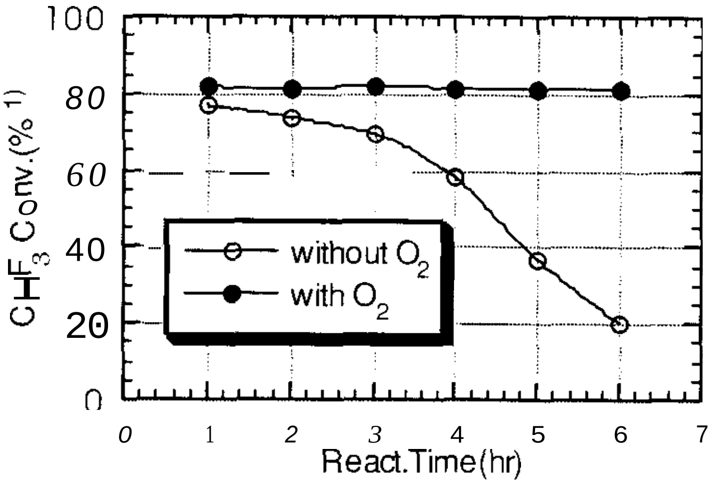
TABLE 3. PRODUCT DISTRIBUTION.

	CF_4	CHF_3	CF_3I	CF_3CF_2I	Others (Perfluoroalkane compounds—$CF_3CF_2CF_3$, etc.)
GC (Area%)	13	*36*	42	*2*	7

$$3CHF_3 + I_2 \xrightarrow{\text{Cat.}} 2CF_3I + 3HF + C \qquad \text{(Reaction 4)}$$

CATALYST LIFE TEST RESULTS

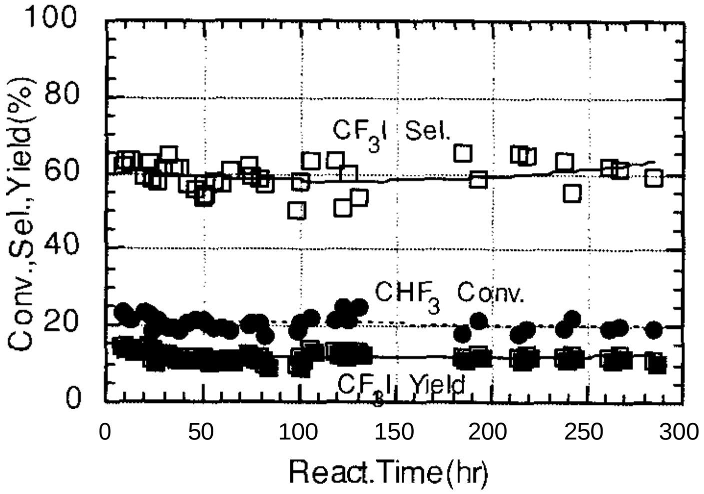
It was found that catalytic activity decreases within a few hours (Figure 1), when tested under accelerated reaction conditions. Therefore, this deactivation would inhibit the industrial acceptance of this process as is. More comprehensive experimentation resulted in finding the culprit, which was coking of the catalyst. The simple solution to the deactivation was to add oxygen to the reaction environment, which prolonged the life of the catalyst. After normalizing the various reaction conditions, the lifetime of the catalyst was significantly improved (Figure 2). The result is a viable commercial process to product CF_3I from CHF_3 by the reaction with I_2 catalytically.



Reaction Condition

	without O_2	with O_2
CHF_3(cc/min.)	100	100
O_2(cc/min)	0	40
I_2/CHF_3(mol ratio)	0.5	0.5
R.Temp.(••)	550	550
SV (hr^{-1})	180	230
Cat.(cc)	100	100

Figure 1. O_2 Effect on the prolongation of catalyst life



Reaction Condition

CHF_3(cc/min.)	
O_2(cc/min)	
I_2/CHF_3(mol ratio)	0.3-0.35
R.Temp.(••)	500-525
SV(hr^{-1})	
Cat.(cc)	100

Figure 2. Results of catalyst life test.

REACTION MECHANISM

As a result of various research activities, such as the components of reaction gas, the analyses of material balances, etc.. it was suggested that this reaction was proceeding to the mechanism shown in Figure **3;** however, it was not completely confirmed until now. Namely. the first step is to eliminate HF from CHF_3. The CF_2 carbene was formed over the catalyst, the CF_2 carbenes were disproportionated, and finally, the CF_3I and compounds having CF_3 group were formed.

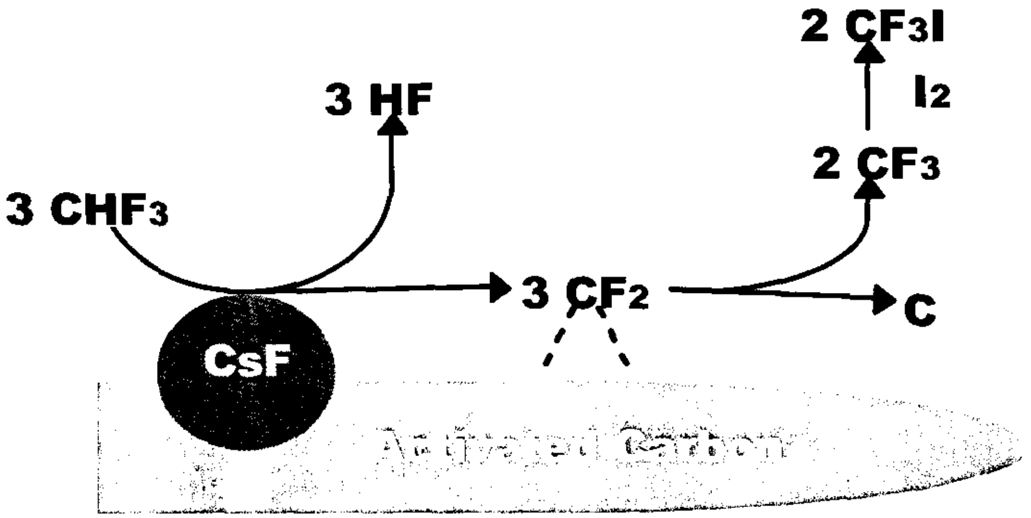


Figure 3. Proposed reaction mechanism.

F-TECH'S CF_3I TECHNOLOGY COMPARED TO OTHER TECHNOLOGIES

We believe that F-TECH's novel technology is superior to older technologies from both a cost and plant efficiency point of view (Table 4). Because the cost of CF_3I relies so heavily on the cost of iodine, it is essential to recover and use waste byproducts. Compared to other known technologies (B) and (C), which involve higher production costs and byproduct disposal problems, the F-TECH's process offers obvious benefits for the continuous production of CF_3I.

TABLE 4. COMPARISON BETWEEN OUR PROCESS AND OTHER ONES.

(A) $CHF_3 + I_2 \longrightarrow CF_3I$ (F-Tech Process)

(B) $CF_3CO_2Na + I_2 \longrightarrow CF_3I + CO_2 + NaI$

(C) $CF_3Br + Zn + ICI \longrightarrow CF_3I + ZnBrCl$

Process	Cost of Raw Materials ($/Kg)	Production System	Advantage	Disadvantage
(A)	14.24	Continuous	Low Raw Material Cost Zero Industrial Waste	Requires Dedicated Plant and Large Capital Investment
(B)	33.24	Batch	Competing Process	High Raw Material Cost Recycle of Nal
(C)	17.66	Batch	Low Raw Material Cost	Special Equipment Disoosal of ZnBrCl

F-TECH'S POSITION TOWARDS COMMERCIALIZATION OF ITS NOVEL CF_3I TECHNOLOGY

While the lower raw material costs and continuous production system of the F-TECH CF_3I technology would indicate superiority over other technologies in use and in the literature, the capital investment required to commercialize our process fully is significant. For that reason, we are researching a number of applications in addition to the potential use of CF_3I as a fire suppressant. These include the following:

- Refrigerant Fluids
- Etchants
- Blowing Agents for Polyurethanes
- Trifluoromethylating agent

To support this effort, F-Tech has constructed a multiton pilot plant at our Nanyo, Japan manufacturing facility for the supply of sample and developmental quantities of CF_3I.

CONCLUSION

As industry and governments move away from the use of halons. which have been shown to be harmful to the earth's ozone layer. CF_3I seems a likely candidate to replace the use of halons in certain applications, particularly in unoccupied areas where CF_3I's suspected cardiotoxicity would preclude or impede its adoption. For prospective CF_3I users, the issue of securing large tonnages at the lowest possible cost is of continuing concern. F-TECH is positioning itself to respond to those concerns and the purpose of this presentation is to bring our activities and capabilities to the attention of this audience.

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