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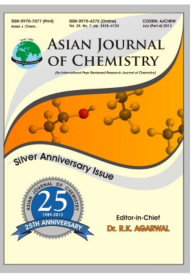

Preparation of Trifluoroiodomethane *via* Vapour-Phase Catalytic Reaction Between Pentafluoroethane and Iodine

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A new route for preparing CF_3I has been developed *via* a reaction between C_2HF_5 and I_2. The influence of reaction temperature and active components of the catalysts on the amount of CF_3I was investigated. The result suggests that the selectivity of the CF_3I can be controlled by reaction conditions and active component of catalyst. The process for the formation of CF_3I and by-products is also discussed.

Key Words: Trifluoroiodomethane, Vapour-phase catalytic, Pentafluoroethane, Difluorocarbene, Trifluoromethyl radical.

INTRODUCTION

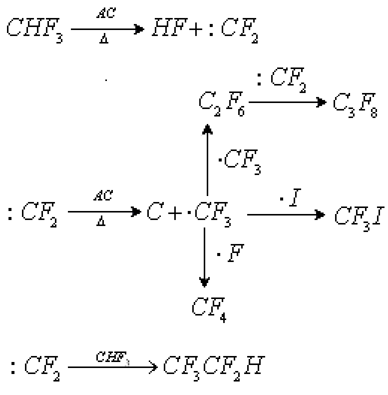
Trifluoroiodomethane (CF_3I) possesses a short atmospheric lifetime and low global warming potential[1,2], which makes it become the preferred alternative for halon and other halohydrocarbons in the application of fire extinguishing agent. Of note, CF_3I is expected for various other applications[3-6], such as freezing medium, etching gas and raw materials for fluorochemicals, *etc*.

Nagasaki *et al*.[7,8] have reported a continuous vapour-phase catalytic process for the manufacture of CF_3I *via* the reaction between trifluoromethane (CHF_3) and iodine (I_2), which makes the CF_3I industrialization possible (**Scheme-I**). Yang *et al.*[9,10] have investigated the above mentioned synthetic mechanism of CF_3I and by products, and suggested that the reaction proceeds *via* difluorocarbenes (CF_2 carbenes) formed on the catalyst surface as intermediates, followed by CF_2 carbene disproportionation to trifluoromethyl (CF_3) radicals, furthermore CF_3 radical react with I_2 to form CF_3I (**Scheme-II**). But the raw material CHF_3 will be stopped little by little based on the montreal protocol, because the global warming potential of CHF_3 is as high as 12000 and the atmospheric lifetime is as long as 250 years. The raw material pentafluoroethane (C_2HF_5) possesses a low global warming potential and the atmospheric lifetime is only 33 years[11].

In our previous report[12], a consideration of the reaction mechanism for the formation of pentafluoroethyl iodide (C_2F_5I) *via* the reaction between C_2HF_5 and I_2 suggested the reaction proceeds also *via* carbenes formed on the catalyst surface as intermediates. Based on this investigation, a new route for preparing CF_3I was developed *via* a vapour-phase catalytic reaction between C_2HF_5 and I_2. We reported here the detailed study on the effect of catalytic activities especially the selectivity of the CF_3I to reaction conditions and catalysts, and the process for the formation of CF_3I and by-products is also discussed.

$$3CHF_3 + I_2 \xrightarrow{cat.} 2CF_3I + 3HF + C$$

Scheme-I



Scheme-II

EXPERIMENTAL

Preparation of catalyst: A commercial wooden AC (Tanxin Activated Carbon Co. Ltd., Shanghai; specific surface area 1322 m^2/g) was used as the catalyst support in this study. After HF (2 M) washing, the AC had an ash content lower than 1.2 wt %, then AC was subjected to 2 M HCl for about 24 h at room temperature in order to decompose the carboxyl and lactone groups, increase the relative amounts of the phenolic and carbonyl groups[13-15], and then the AC was washed with distilled water and dried in air at 103-105 ºC overnight. After that, the sample was added to the aqueous metal salts solution, impregnated at room temperature for about 6 h and dried by a rotary evapourator at about 80 ºC for 4 h. The pre-dried catalyst was then calcined at 600 ºC for 2 h under nitrogen flow.

Synthesis of CF_3I: 15 mL catalysts were packed into a fixed bed reactor and were heated to 550 ºC under nitrogen. Then nitrogen flow was stopped and C_2HF_5 was introduced to reactor at a rate of 60 mL/min. After 2 h, I_2 was provided by bubbling C_2HF_5 into molten I_2 which was placed in a stainless steel evaporator and heated up to 190 ºC in an oil bath. The products were neutralized by $Ca(OH)_2$ solution, dried with $CaCl_2$ and analyzed by GC-MS. The results were listed as follows:

1. CF_4, *m/z*: 69, $^+CF_3$; 50, $^+CF_2$; 31, ^+CF; 19, ^-F.
2. CF_3CF_3, *m/z*: 119, $^+CF_3CF_2$; 100, $^+CF_2CF_2$; 69, $^+CF_3$; 50, $^+CF_2$; 31, ^+CF.
3. CHF_3, *m/z*: 69, $^+CF_3$; 51, $^+CHF_2$; 31, ^+CF.
4. $CF_3CF_2CF_3$, *m/z*: 169, $^+CF_3CF_2CF_2$; 119, $^+CF_3CF_2$; 100, $^+CF_2CF_2$; 69, $^+CF3$; 50, $^+CF_2$; 31, ^+CF.
5. CF_3I, *m/z*: 196, $^+CF_3I$; 177, $^+CF_2I^+$; 127, ^-I; 69, $^+CF_3$; 31, ^+CF;
6. CF_3CF_2I, *m/z*: 246, $^+CF_3CF_2I$; 227, $^+CF_2CF_2I$; 177, $^+CF_2I^+$; 158, ^+CFI; 127, ^-I; 119, $^+CF_3CF_2$; 100, $^+CF_2CF_2$; 69, $^+CF_3$; 50, $^+CF_2$; 31, ^+CF.

Characterization of samples: Products were analyzed by means of GC-1002 produced by Beijing analytical instrument factory. The capillary column was a CP-PoraPLOTQ with 0.32 mm diameter and 30 m length from J & WScientific Inc. The column was programmed as follows: the initial temperature was set at 60 ºC for 6 min; then the temperature was increased at the rate of 40 ºC/min and finally reached to 200 ºC and held for 11 min. The instrumental parameters were set up as follows: injection port temperature, 200 ºC; FID detector, 250 ºC; the carrier gas was N_2 (0.1 MPa). The products were identified by comparison of their GC retention times and mass spectra with authentic samples. Quantitative analysis of the product standard ratios was obtained by comparison with mixtures prepared for calibration purposes. The relative response coefficients and retention time of each compound are given in Table-1.

TABLE-1
RELATIVE RESPONSE COEFFICIENTS
($k_I/_{kstd}$) DETERMINED BY GC-FID

Sample	Retention time/min	$k_I/_{kstd}$
CHF_3	8.3	3.6
CF_3CHF_2	8.5	1.0
CF_3I	9.5	1.45
C_2F_5I	10.4	1.29

GC-MS (EI, 70 eV) spectra were measured using the Shimazu GCMS-QP2010 system equipped with GC-2010. The column was CP-PoraPLOT Q with 0.32 mm i.d. and 30 m length from J & W Scientifc Inc. The column was programmed as above-mentioned GC conditions. Injection port temperature, 200 ºC; the carrier gas rate, 4.1 cm^3 He/min.

RESULTS AND DISCUSSION

Synthesis of CF_3I on different temperature: Effect of the reaction temperature on product distribution in the gas-phase catalytic reaction for the synthesis of CF_3I between C_2HF_5 and I_2 in the presence of K_2CO_3/AC catalyst was examined. The results were shown in Fig. 1 and the product distribution was listed in Table-2.

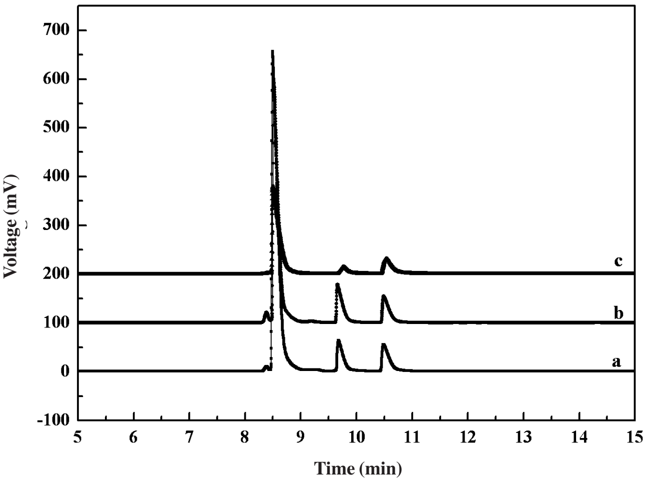


Fig. 1. GC spectrum of gas products; a-reaction at 500 ºC, b- reaction at 550 ºC, c- reaction at 600 ºC

TABLE-2
EFFECT OF REACTION TEMPERATURE
ON PRODUCT DISTRIBUTION

Temperature (ºC)	Ratio of relative volume of products (%)				
	C_2HF_5	CHF_3	CF_3I	C_2F_5I	Others
450	100	-	-	-	-
500	79.4	1.4	8.4	10.1	0.7
550	68.7	0.4	17.2	13.7	-
600	68.2	1.2	8.9	19.8	1.9

- -no products detected

The conversion of C_2HF_5 increased with the increasing reaction temperature and when the reaction temperature was 450 ºC, reaction did not occur and only raw material C_2HF_5 was detected in gas product. When the reaction temperature was 550 ºC, the conversion of C_2HF_5 reached 31.3 % and CF_3I was produced in 17.2 % relative volume of the gaseous products for 4 h, accompanying with CF_4, CHF_3, C_2F_6, C_3F_8 and C_2F_5I as by-products. But the ratio of CF_3I formed gradually decreased when the reaction temperature was 600 ºC, the concentration of CF_3I reached only in 8.4 % (Table-2). It is suggested that the selectivity of the CF_3I is controlled by reaction conditions.

Synthesis of CF_3I on different catalysts: The tested catalysts were made from various alkali metal salts and alkaline earth metal salts with AC as a supporter. The catalytic activities of these catalysts were tested after 4 h reaction (Table-3).

TABLE-3
EFFECTS OF ALKALI METAL AND ALKALINE EARTH METAL SALT CATALYSTS ON THE REACTION OF C_2HF_5 AND I_2

Component	C_2HF_5 conversion (%)	CF_3I selectivity (%)	C_2F_5I selectivity (%)
$NaNO_3$	11.2	0	0
KNO_3	18.7	53.5	29.0
$RbNO_3$	30.4	44.0	40.0
$CsNO_3$	17.3	36.5	32.5
KF	22.0	49.5	48.7
RbF	18.5	34.0	51.3
CsF	<1	0	0
K_2CO_3	31.3	54.9	43.8
$Mg(NO_3)_2$	5.9	13.6	12.4
$Ba(NO_3)_2$	9.8	20.1	11.9

Reaction temperature: 550 ºC; C_2HF_5/I_2 (mol ratio):1.5; SV: 130 h^{-1}

As shown in Table-3, alkali metal salts shows a higher catalytic activity than the alkaline earth metal salts. This is because the electronegativity of alkali metal is less than the alkaline earth metal and the basicity of the alkali metal oxide decomposing from alkaline metal is better than alkali earth metal oxide decomposing from alkaline earth metal. Zhu *et al.*[16] have reported that the decomposition of alkaline earth metal nitrates becomes more difficult with the atomic number increases. The highest activity of the alkali metal catalysts is $RbNO_3$ and the highest selectivity is potassium such as KF and K_2CO_3. While the anions, counterion to the metal cations, have also effect on the reaction rate, NO_3^- with high selectivity and F^- with high activity.

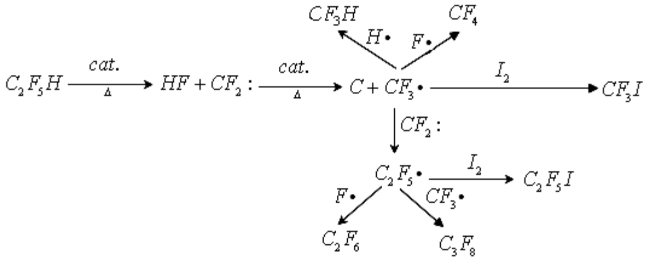
Based on exhaustive studies, it is found that the most suitable catalyst for this reaction is the synergistic combination of KF with high selectivity and $RbNO_3$ with high activity, especially the mass ratio of $RbNO_3$ and KF is 3:1(Table-4). This ensures that the selectivity of the CF_3I is also controlled by active component of catalyst.

TABLE-4
EFFECT OF THE RATIO OF TWO ACTIVE COMPONENTS ON CATALYTIC ACTIVITY

$KF/RbNO_3$ (mass ratio)	C_2HF_5 conversion (%)	CF_3I selectivity (%)	C_2F_5I selectivity (%)
1:1	34.6	50.2	32.5
1:2	46.0	42.4	41.2
2:1	40.0	43.8	39.3
1:3	46.5	53.1	28.3
3:1	38.3	51.2	32.8

Reaction temperature: 550 ºC; C_2F_5H/I_2 (mol ratio):1.5; SV: 130 h^{-1}

The compounds containing CF_3 group such as CHF_3, CF_4, C_2F_6, C_3F_8, C_2F_5I and CF_3I were formed. We propose the following process for the formation of CF_3I and by products. As shown in **Scheme-III**, C_2HF_5 is decomposed to form the intermediates CF_2 carbene. Then CF_2 carbene is absorbed on the surface of the catalysts and disproportionation to CF_3 radicals, furthermore CF_3 radical react with I_2 to form CF_3I, whereas with H and F to form CHF_3 and CF_4. H radical[17-19] maybe comes from carboxyls and phenols on the AC surface and F radical[9] comes from the decomposing of CF_2 carbene on heat. Alternatively, CF_3 radical reacts with CF_2 carbene to form CF_3CF_2 radical, which generates C_2F_5I, C_2F_6 and C_3F_8.



Scheme-III: Suggested process for the formation of CF_3I and by-products

Conclusion

A new method for the preparation of CF_3I has been developed *via* a reaction between C_2HF_5 and I_2. The effect of the temperature on the synthesis of CF_3I was studied and the results indicated that the conversion of C_2HF_5 increased with the increasing reaction temperature, but the radio of CF_3I formed gradually decreased. Also the conversion of C_2HF_5 and the selectivity of CF_3I reached 46.5 % and 53.1 % respectively when the reaction was conducted in the presence of Rb-K/AC catalyst with the mass ratio of 3:1 ($RbNO_3$:KF). The results suggest that the selectivity of the CF_3I can be controlled by reaction conditions and active component of catalyst. Furthermore, the catalyst promotes disproportionation of CF_2 carbene to generate CF_3 radical, which reacts with I_2 to form CF_3I.

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