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Interaction of Trichloromethane and Tetrachloromethane with Nitrogen Trifluoride

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Abstract—Interaction of nitrogen trifluoride with trichloromethane and tetrachloromethane at temperatures in the range from 20 to 200°C and pressures of up to 6.0 MPa in the gas and liquid phases was studied.

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One of the most important problems in the technique for synthesis of nitrogen trifluoride NF_3 by fluorination of a melt of acid ammonium bifluoride salts with fluorine is purification of the target product to remove trifluoromethane CF_4 . A method based on the different solubilities of these gases in a number of fluids has been suggested for separation of NF_3 and CF_4 by absorption. It has been shown that tetrachloromethane and trichloromethane are absorbents satisfying a number of technological and economical requirements [1].

To develop an industrial technology for purification of nitrogen trifluoride to remove tetrafluoromethane by the above method, it is necessary to evaluate the reactivity of the suggested absorbents toward NF₃, which is a fluorinating agent under certain conditions [2]. A study of this kind is necessary for solution of problems related to, first, provision of a safe operation of equipment, second, to determination of gaseous impurities that appear in nitrogen trifluoride upon its contact with the absorbent, and, third, to estimation of the service life of the absorbent.

No data on the nature of interaction between nitrogen trifluoride (NTF) and chloromethanes could be found in the literature, and, therefore, the goal of our study was to experimentally examine the interaction of trichloromethane and tetrachloromethane with nitrogen trifluoride under various conditions.

Interaction of chlorocarbons with fluorinating agents. As an analog in development of a model of

interaction between nitrogen trifluoride and absorbents can serve mechanisms described in the literature for reactions between other fluorinating agents and chloromethanes and the fluorinating properties of NF₃.

There are various processes of interaction between trichloromethane and a fluorinating agent: fluorination with hydrogen fluoride in the liquid phase at $60-100^{\circ}$ C and a pressure of 3.1 MPa [3, 4], gas-phase catalytic method [4], and fluorination of trichloromethane with antimony trifluoride in the presence of antimony pentafluoride at 100°C and a pressure of 5.89 MPa [5]. In these processes, the reaction occurs with successive substitution of chlorine atoms with fluorine, with predominant formation of dichlorofluoromethane CHCl₂F. Tetrafluoromethane has been found as a main product only upon interaction of fluorine diluted with nitrogen with trichloromethane and tetrachloromethane in the combustion mode [6].

According to [6], many processes of interaction between tetrachloromethane and fluorinating agents are similar to processes involving trichloromethane. The reaction of fluorination of tetrachloromethane with higher fluorides of variable-valence metals and, in particular, with cobalt trifluoride yields compounds appearing in Eq. (1) [7, 8]:

$$4\text{CCl}_4 + 12\text{CoF}_3 \rightarrow \text{CCl}_2\text{F}_2 + 2\text{CClF}_3 + \text{CF}_4 + 12\text{CoF}_2 + 6\text{Cl}_2.$$
(1)

At low temperatures (up to 300°C), nitrogen trifluoride behaves in reactions as a passive oxidizing agents [2]. In contrast to other nitrogen fluorides, this

compound does not react with an aqueous solution of potassium iodide at room temperature. At low temperatures, only a single fluorine atom is reactive in the nitrogen trifluoride molecule, and NF₂ radical is transformed into tetrafluorohydrazine upon dimerization.

Depending on the number of fluorine atoms abstracted from the nitrogen trifluoride molecule (one, two, or three), the possible reaction products are, respectively, tetrafluorohydrazine N_2F_4 , difluorodiazines N_2F_2 , and nitrogen. Because difluorodiazines decompose at above 70°C into nitrogen and fluorine, the remaining reaction products are tetrafluorohydrazine and nitrogen [2]. The most important reaction with nitrogen trifluoride is its conversion into tetrafluorohydrazine:

$$NF_3 + M \to N_2F_4 + MF_n. \tag{2}$$

A number of substances: carbon, mercury, copper, iron, nitrogen oxide, and sodium chloride have been suggested as fluorine acceptors M [9, 10].

Thus, we can conclude that the main process in fluorination of chloromethanes is the successive substitution of chlorine atoms with fluorines. A hydrogen atom is commonly the last to be substituted or is substituted under very severe conditions, at temperatures higher than 500°C or with a strong fluorinating agent (fluorine, chlorine trifluoride). In the process, dimerization of radicals is possible.

In fluorination at temperatures below 300° C, nitrogen trifluoride commonly donates a fluorine atom, with tetrafluorohydrazine formed. Thus, the main products formed in fluorination of trichloromethane and tetrachloromethane with nitrogen trifluoride will probably be tetrafluorohydrazine, chlorine, and dichlorofluoromethane CHCl₂F for the first of the absorbents, and trichlorofluoromethane CCl₃F for the second. In addition, also possible is formation of smaller amounts of chlorodifluoromethane CHCl₂F₂, and other chlorofluoromethanes. Deeper fluorination to give tetrafluoromethane, nitrogen, and chlorine is only possible at higher temperatures.

In the technological process for purification of nitrogen trifluoride to remove tetrafluoromethane, an absorbent and NF_3 will come in contact both in the liquid phase, when the gas being purified is dissolved in a fluid, and in the gas phase, in which there is absorbent vapor. The rates of the gas- and liquid-phase processes may substantially differ. Therefore, it is

necessary to perform experimental studies for both the processes. It follows from the technological parameters of the absorption purification of nitrogen trifluoride and from its physicochemical properties that the temperature and pressure at which NF₃ and chloromethanes can interact will not exceed 200°C and 6 MPa. To these values was limited the range of our experimental study.

Interaction of trichloromethane and nitrogen trifluoride in the liquid phase. The interaction of nitrogen trifluoride and trichloromethane was studied on an experimental installation by the method described in [1] in the isobaric-isothermal mode. The reaction duration was up to 96 h. Several samples were taken from the gas and liquid phases. After the liquid phase was sampled, gas was desorbed from the absorbent and the gas and absorbent were analyzed.

A gas-chromatographic analysis procedure that can most fully determine the content of chlorofluoromethanes was reported in [1]. The retention time of trichloromethane was not specified, but we found by making test analyses that this component can be detected by this method and determined the relative retention time.

Table 1 lists relative retention times of the components and their minimum determinable concentrations in conformity with GOST (State Standard) 19212–87 [11] and those experimentally measured with a Kristall-2000M chromatograph.

The liquid phase was analyzed in accordance with GOST 20015–88 [12], the presence of tetrafluorohydrazine in a sample was determined and its concentration was measured by the method described in [13].

In conformity with GOST 20015–88 [12], trichloromethane is delivered to consumers with addition of a stabilizer whose role was played by ethanol in an amount of up to 1 wt %. Trichloromethane manufactured by Khimprom Volgograd Open Joint-Stock Company, with addition of 0.5 wt % ethanol, was used in our experiments.

The experiments were performed at temperatures of 20 to 150°C and pressures of 5.5–6.5 MPa. No special treatment of the inner surface of the reaction vessel was carried out. No impurities were detected at the analysis procedure sensitivity in gas samples taken at temperatures of up to 110°C taken both directly from the reactor and from the liquid upon desorption of the



Fig. 1. Amount *X* of dichlorofluoromethane formed in the gas phase vs. the residence time τ of reagents in the interaction of trichloromethane stabilized with (*I*–3) ethanol and (4) 0.05 wt % amylene with nitrogen trifluoride in the liquid phase. Temperature (°C): (*I*) 111, (2) 135, (3) 152, and (4) 149. Pressure (MPa): (*I*) 6.5, (2) 6.4, (3) 5.6, and (4) 5.3.

gas. In gas samples taken at temperatures of 110 to 150° C, only an admixture of dichlorofluoromethane CHCl₂F was found. An analysis of the liquid phase did not reveal any changes in the composition of trichloromethane, compared with the starting substance. The parameters of the experiments and the amount of dichlorofluoromethane in samples taken from the gas phase of the reactor and from the gas desorbed from the liquid are presented in Fig. 1.

Specialists from the manufacture plant suggested to use amylene, a mixture of pentene isomers, as a stabilizer for trichloromethane. The advantage provided by the replacement of ethanol with amylene is in that the stabilizing effect is provided by introduction of a smaller amount of the stabilizer (0.01 to 0.1 wt %)into trichloromethane. Therefore, we prepared a sample containing 0.05 wt % amylene. An experiment was performed with this sample, and the results obtained are presented in Fig. 1, straight line 4. It can be seen that the rate of trichloromethane fluorination with nitrogen trifluoride is almost the same with 0.5 wt % ethanol or 0.05 wt % amylene used as a stabilizer.

The appearance of dichlorofluoromethane in the products of interaction between nitrogen trifluoride and trichloromethane is evidence in favor of the following scheme of the fluorination process:

$$2CHCl_3 + 2NF_3 \rightarrow 2CHCl_2F + N_2F_4 + Cl_2.$$
(3)

To determine whether tetrafluorohydrazine is present in gas samples, we performed a mass-spectrometric analysis with a MI-1309 instrument. The analysis revealed the presence of trace amounts of N_2F_4 in the samples.

Because the suggested reaction scheme could not be reliably confirmed by the results of the experiments described above, we carried out more prolonged experiments at higher temperatures. For this purpose, we changed the experimental procedure by placing the reactor filled with trichloromethane and NF_3 in an air thermostat heated to the working temperature.

The experiment was performed under the following conditions: temperature 165°C, pressure 5.6 MPa, residence time 96 h, chloroform with 0.05 wt % amylene. The following results were obtained: content of dichlorofluoromethane in the gas phase of the reactor, 0.233 vol %, and that in the gas upon the desorption state, 0.031 vol %. In addition, N_2F_4 was

Reagents and fluorination products of tri- and tetrachloromethanes with nitrogen trifluoride	Relative retention time	Minimum determinable c, vol %	
		by the method from [11]	experiment
Air (NTF)	0.59	0.015	n.f ^a
Trifluorochloromethane	0.69	0.007	n.f ^a
Difluorochloromethane	1.65	0.019	n.f ^a
Fluorotrichloromethane	2.50	0.095	0.002
Fluorodichloromethane	4.42	0.034	0.002
Carbon tetrachloride	8.00	0.013	n.f ^a
Chloroform	10.82	b	0.003

Table 1. Relative retention time of chloromethanes and fluorochloromethanes and their minimum determinable concentrations

^a n.f., substances not found in a sample; the same for Tables 2–4. ^b Absent in the procedure from [11].



Fig. 2. Schematic of a laboratory installation for studies of the interaction between chloroform and nitrogen trifluoride in the gas phase. (1) Cylinder with NTF, (2) vessel for preparation of a gas mixture of NTF and chloroform, (3) gas-phase reactor, (PG) pressure gages, and (CV) control valves.

found in the gas phase in an amount of 0.06–0.08 vol %. No other impurities were found in the liquid phase.

To determine the fluid composition from the last experiment with a higher precision, we performed a chromato-mass-spectrometric analysis of a sample on a Hewlett–Packard GC5890-MSD 5972A instrument. It was found that amylene is entirely absent in chloroform after its reaction with nitrogen fluoride and there appear products formed in chlorination of amylene: dichloropentane, 1-chloro-2-methylbutene, 2-chloro-2,3-dimethylbutane, etc. In addition, the sample contained trace amounts of hexachloroethane and fluorotrichloromethane. When determining molecular chlorine, we found that its concentration in the liquid phase is 0.013 wt %.

Thus, our experiments demonstrated that chloroform and nitrogen trifluoride interact in the liquid phase by scheme (3). The resulting chlorine enters into the reaction with the stabilizer, amylene, to give organochlorine compounds. No other impurities were found in chloroform.

Interaction of trichloromethane and nitrogen trifluoride in the gas phase. To study the fluorination of trichloromethane with nitrogen trifluoride in the gas phase, we modified the laboratory installation and the experimental procedure. The modified laboratory installation is shown schematically in Fig. 2. The reactor for gas-phase fluorination had the form of a tube with an inner diameter of 12 mm, length of 700 mm, and volume of 66 cm³. The reactor was made of 12Kh18N10T stainless steel. Because nitrogen fluoride reacts with metals to give tetrafluorohydrazine [2], the reactor walls were preliminarily passivated with fluorine.

The study was performed in the following way. Nitrogen trifluoride was bubbled through a vessel filled with liquid trichloromethane and thereby was saturated with a trichloromethane vapor. The mixture was delivered into the reactor for gas-phase fluorination. The pressure in the vessel was chosen so that the equilibrium concentration of the trichloromethane vapor was 4-6 vol % at a given temperature. The mixture of NF₃ and the absorbent vapor was passed through the reactor at a prescribed temperature under atmospheric pressure. Samples for a gas-chromatographic analysis were taken at the reactor outlet.

To determine the effect of the stabilizer vapor on the gas-phase fluorination of trichloromethane, we

$T, ^{\circ}\mathrm{C}$ CHCl ₃ composition	Formation rate, vol % h^{-1}			
	CHCl ₂ F	$C_2H_2Cl_4$	CCl ₄	
127	Unstabilized	0.008	_	_
153		0.023	_	_
169		0.041	0.006	0.006
180		0.128	0.061	0.018
138	Stabilized with 1 wt % ethanol	0.005	0.003	-
158		0.011	0.012	_
170		0.037	0.015	_
183		0.095	0.032	_
149		0.009	0.012	_
161	Stabilized with 0.05 wt % amylene	0.021	0.089	0.003
172		0.069	0.096	0.005
187		0.166	0.090	0.004

Table 2. Variation of the impurity formation rates with temperature in the gas-phase fluorination of trichloromethane with nitrogen trifluoride

performed experiments both with an unstabilized substance and with that stabilized with 1 wt % ethanol or 0.05 wt % amylene. The experiment parameters and rates of impurity formation under prescribed conditions are listed in Table 2.

It can be seen in Table 2 that reaction products contain noticeable amounts of tetrachloroethane whose appearance is impossible if trichloromethane is fluorinated by the scheme described by Eq. (3). Based on the results obtained, we suggested the following chain fluorination mechanism including the stage of heterogeneous chain initiation at active centers of the reactor wall:

$$\operatorname{CHCl}_3 + \operatorname{M}^* \to \operatorname{CHCl}_2^* + \operatorname{Cl}^* + \operatorname{M}, \qquad (4)$$

$$2CHCl_2^* + 2NF_3 \rightarrow 2CHCl_2F + N_2F_4, \qquad (5)$$

$$\operatorname{CHCl}_{2}^{*} + \operatorname{CHCl}_{2}^{*} \to \operatorname{C}_{2}\operatorname{H}_{2}\operatorname{Cl}_{4}, \tag{6}$$

$$\mathrm{Cl}^* + \mathrm{Cl}^* \to \mathrm{Cl}_2. \tag{7}$$

It is the occurrence of a heterogeneous chain initiation that leads to a nearly an order-of-magnitude

Table 3. Effect of temperature on the impurity formation rate in the gas-phase fluorination of trichloromethane with nitrogen trifluoride in reactor B, unpassivated and with apparatus walls passivated with fluorine

T,°C	CHCl ₃ composition	Formation rate, vol % h^{-1}		
		CHCl ₂ F	$C_2H_2Cl_4$	CCl ₄
Unpassivated reactor				
147		0.105	0.047	0.006
164	Unstabilized	0.880	0.337	0.013
129	Stabilized	0.046	0.024	n.f.
171	with 0.5 wt % ethanol	0.807	0.439	0.009
132	Stabilized	0.059	0.038	n.f.
153	with 0.05 wt % amylene	0.255	0.064	0.006
	Passiv	ated reactor		
133		0.005	0.002	n.f.
165	Unstabilized	0.034	0.009	0.003
152	Stabilized	0.010	0.008	_
176	with 0.5 wt % ethanol	0.039	0.013	0.008
142	Stabilized	0.006	0.002	n.f.
155	with 0.05 wt % amylene	0.011	0.003	n.f.

increase in the rate of impurity formation, compared with the liquid-phase fluorination of trichloromethane, in which the process occurs only by scheme (3). The presence of an insignificant amount of difluorochloromethane in samples is in good agreement with the hypothesis of a successive substitution of chlorine atoms with fluorines. The experimental results in Table 2 demonstrate that the gas-phase fluorination of trichloromethane is not affected by the absence or presence of a stabilizer and its type. A probable reason is that the stabilizer concentration in the gas phase is very low.

To confirm the suggested fluorination mechanism of trichloromethane, we studied the influence exerted by the geometric characteristics of the apparatus (its surface area-to-volume ratio) and by a preliminary treatment of the apparatus surface with fluorine (passivation). For this purpose, we performed a series of experiments in a reactor with the following geometric parameters: inner diameter 20 mm; length 160 mm; volume 50 cm³; and ratio between the surface area of the apparatus to its volume, $1.0 \text{ cm}^2/\text{cm}^3$ (5.7 cm²/cm³ in the preceding series of experiments). The first reactor is denoted in the text by symbol A, and the second, B.

Table 3 lists the results of experiments on trichloromethane fluorination in an unpassivated reactor B and upon passivation of the apparatus with fluorine.

Comparison of the experimental results in Tables 2–4 suggests that the rate of impurity formation in fluorination of trichloromethane in the gas phase is the most strongly affected by processes occurring at the apparatus surface. In the case of the unpassivated reactor surface, the maximum impurity formation ate is observed. For example, dichlorofluoromethane, the main product of chloroform fluorination, is formed in an unpassivated reactor at the same temperature in an amount exceeding by nearly an order of magnitude that in the reactor preliminarily treated with fluorine. Moreover, a decrease in the specific surface area of the apparatus also leads to a lower rate of the fluorination reaction. All this confirms the validity of the abovesuggested mechanism of trichloromethane fluorination by nitrogen trifluoride in the gas phase, which includes the heterogeneous stage of chain initiation.

To determine how pressure affects the rate of impurity formation in the gas-phase process, we carried out experiments by the above-described procedure at pressures of 1.2 and 3.7 MPa. The results obtained demonstrate that raising the pressure to 3.7 MPa has no significant effect on the fluorination of trichloromethane in the gas phase.

Interaction of tetrachloromethane with nitrogen trifluoride in the gas phase. It was shown in the experiments with trichloromethane that the rate of impurity formation in the liquid phase is substantially lower than that in the gas phase, Therefore, we experimentally studied only the gas-phase fluorination of tetrachloromethane by nitrogen trifluoride. The experiments were carried out on the same installation and by the same procedure as those in the case of trichloromethane under atmospheric pressure in reactor B. Because trichlorofluoromethane, dichlorofluoromethane, tetrafluorohydrazine, and chlorine must be formed as products in fluorination of tetrachloromethane, the methods described above can be used for analysis of these substances [11, 13]. We used tetrachloromethane of pure grade (GOST 20288-74 [14]. Table 4 lists the results of experiments on tetrachloromethane fluorination in the gas phase.

Table 4. Effect of temperature on the impurity formation

 rate in the gas-phase fluorination of tetrachloromethane with

 nitrogen trifluoride

<i>T</i> ,°C	Formation rate, vol % h ⁻¹		
	CCl ₃ F	$C_2 Cl_6$	
127	0.002	n.f.	
148	0.008	n.f.	
164	0.056	0.009	
182	0.155	0.023	
197	0.958	0.096	

It can be seen that the gas-phase fluorination of tetrachloromethane with trifluoride nitrogen occurs by a similar mechanism, with the formation rates of the main impurities, trichlorofluoromethane for tetrafluoromethane and dichlorofluoromethane for trichloromethane, nearly coincide under similar conditions in the temperature range 120–180°C.

CONCLUSIONS

(1) A study of the interaction of nitrogen trifluoride with tetrachloromethane and trichloromethane demonstrated that, at temperatures below 110°C and pressures of up to 6 MPa, the reaction rate is such that fluorination products can be found neither in the gas phase, nor in the liquid phase at contact duration on the order of 100 h.

(2) At temperatures higher than 110°C, the main products formed in fluorination of trichloromethane and tetrachloromethane are, respectively, fluorodichloromethane and fluorotrichloromethane, with tetra-fluorohydrazine and molecular chlorine formed as byproducts.

(3) The rate of trichloromethane fluorination in an apparatus passivated with fluorine is an order of magnitude lower that in an unpassivated equipment, which is accounted for by the occurrence of the reaction by the radical mechanism with heterogeneous chain initiation on the metallic surface of the reactor.

(4) When industrially manufactured stabilizercontaining chloroform interacts with nitrogen trifluoride in the liquid phase, the process of a chemical transformation of the stabilizer occurs in the first place. Therefore, it can be recommended to use in the industry trichloromethane stabilized with amylene, whose amount can be minimized to 0.01 wt %.

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