November, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***60***, *3979—3983 (1987)*

Fe_3O_4-Catalyzed Halogen-Exchange Reactions of Polyhalomethanes

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(Received June 5, 1987)

Triiron tetraoxide pretreated by polyhalomethane was shown to catalyze the halgen-exchange reactions of polyhalomethanes $CH_lBr_mCl_n(l=1$ or 2). The exchange proceeds consecutively giving, for example, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ as the main products from $CHCl_3$. The mechanism of the reaction is discussed briefly.

In recent decades, the contamination of environment with polyhalogenated compounds have induced serious problems in several countries.[1)] Thus, thermal and photochemical behaviors of polyhalogenated hydrocarbons have been investigated rather extensively aiming the potential applications for their detoxication.[2—5)] We have also studied the acid-catalyzed and the photochemical dehalogenation and rearrangement of polyhalobenzenes in this point of view.[6—8)] One of our studies concerned with the dechlorination of polychlorobenzenes over Fe_3O_4.[9)] This modification of iron oxide was shown to catalyze the cleavage of carbon-halogen bonds of polyhalobenzenes effectively and gave the dehalogenated products in the presence of hydrogen donor such as hexane and decahydronaphthalene.

In this paper, we wish to report on the halogen-exchange reactions of polyhalomethanes over Fe_3O_4 in order to clarify further the behaviors of Fe_3O_4 towards halogenated hydrocarbons.

Experimental

Materials. The polyhalomethanes were commercially available. Their purities were certified by gas chromatography. Triiron tetraoxide (magnetite, Fe_3O_4) was prepared according to the method described by Kiyama.[10)] Firstly, 6 M[††] aqueous solution of sodium hydroxide was added gradually to an aqueous solution containing iron(II) and iron(III) chlorides in a 1:2 molar ratio so as to regulate the final pH of the solution to be ca. 11. The suspension of colloidal iron hydroxides was then filtered, washed with several portions of water, and calcinated at 623 K. Active Fe_3O_4 thus obtained is very fine and its specific surface area was determined to be 92.6 $m^2\,g^{-1}$ by the BET adsorption measurement. Thus prepared Fe_3O_4 was employed as the catalyst for the halogen-exchange reactions. In each run of the halogen-exchange reaction, a 300 mg portion of the Fe_3O_4 catalyst was pretreated at 623 K with 50 microliter of chloroform or bromoform in the stream of helium. In order to maintain the catalytic activity uniform throughout a series of the experiments, the catalyst was heated further at the same temperature for about 2 h until the evolution of hydrogen halide ceased completely.

Procedures for the Pulse Thermolysis and the Analyses of the Products. The reaction was carried out at temperatures ranging from 393 to 593 K using a pulse micro-reactor connected directly to a gas chromatograph. The sample was introduced in portions of 1 microliter to the thermostatic inlet connected to the reaction chamber containing 300 mg of Fe_3O_4 and carried to the reactor by a stream of helium. The products of the reaction were analyzed by a Shimadzu GC-4C PTF gas chromatograph using a 2 m stainless steel column containing DNP (20 wt%). Peaks on the chromatogram were identified by comparing them with those of authentic samples and by GC/MS measurements. GC/MS were recorded on a Shimadzu GC/MS QP 1000 mass spectrometer. Details of the apparatus for the reaction were described in one of our previous papers.[11)]

Results and Discussion

Role of the Pretreatment with Polyhalomethane and the Mechanism of Halogen Exchange. When polyhalomethanes were treated with freshly prepared Fe_3O_4 at 623 K without prior treatment with trihalomethanes, the oxidative decomposition took place giving carbon dioxide and water. Thus the reaction is potentially applicable to the detoxication of polyhaloalkanes. Hydrogen halide (HCl or HBr) was not detected as a gaseous product in the process of these reactions when the catalyst is new. The oxidative decomposition reaction seemed to proceed irreversibly, and repeated feeds of polyhalomethane gradually reduce the catalytic activity of Fe_3O_4 for the oxidative decomposition. Deactivation of the catalyst is undesirable from the view point of applying the reaction to the detoxication. Thus the reactions over polyhalomethane-poisoned Fe_3O_4 were further studied. The peak for the unreacted starting material becomes observable in the chromatogram after several repetition of the pulse reaction with polyhalomethanes (dichloromethane (**1**), trichloromethane (**3**), dibromomethane (**6**), and tribromomethane (**7**)). At the same time, evolution of hydrogen halide became observable after repeated dose of polyhalomethane. When a mixed halomethane $CH_lCl_mBr_n$ was fed under similar conditions or when polybromomethane was introduced over polychloromethane-pretreated Fe_3O_4 (or vice versa), there appeared several other peaks ascribable to the products of halogen-exchange reactions in the gas chromatogram. An example

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[††] $1\ M=1\ mol\,dm^{-3}$.

which shows the formation of $CHCl_3$, $CHBrCl_2$, and $CHBr_2Cl$ from $CHBr_3$ is illustrated in Fig. 1. This reveals the fact that the pretreated catalyst promotes the halogen exchange of polyhalomethanes. The activity of the Fe_3O_4 catalyst for the oxidative decomposition tends to be a constant stationary value when the total dose of **1** or **3** exceeds ca. 0.2 mmol (ca. 20 microliter) (Fig. 2).[12] At this stage, the formation of iron(II) chloride on the surface of the catalyst was evidenced by detecting iron(II) ion from the aqueous extract obtained by washing the pretreated catalyst with water. Chloride ion, and/or bromide ion in cases when bromo-substituted methane was subjected to the reaction, was also present, but iron(III) ion was detected in neither cases. Thus the oxidative decomposition should proceed via the reductive chlorination of Fe(III) oxide. As a result, the surface of Fe_3O_4 is expected to become covered partly by iron(II) chloride in the process of pretreatment by polychloromethanes, and similarly covered by iron(II) bromide when treated with polybromomethanes. The pretreated catalysts were used for the halogen-exchange reactions throughout this series of experiments. The catalyst regains its reactivity for oxidative

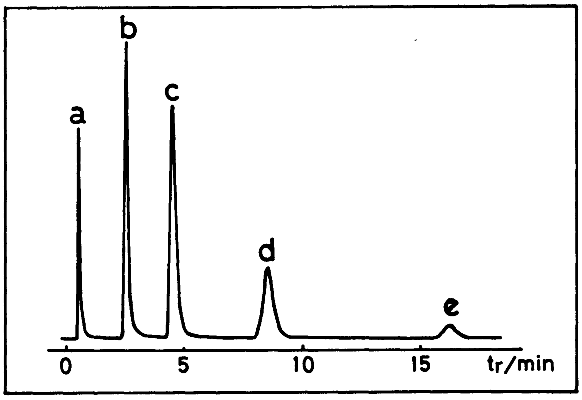

Fig. 1. Gas chromatogram of the reaction products obtained by introducing $CHBr_3$ over Fe_3O_4 (pretreated by $CHCl_3$) at 433 K. Peaks **a**—**e** are assigned to CO_2, $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and unreacted $CHBr_3$, respectively.

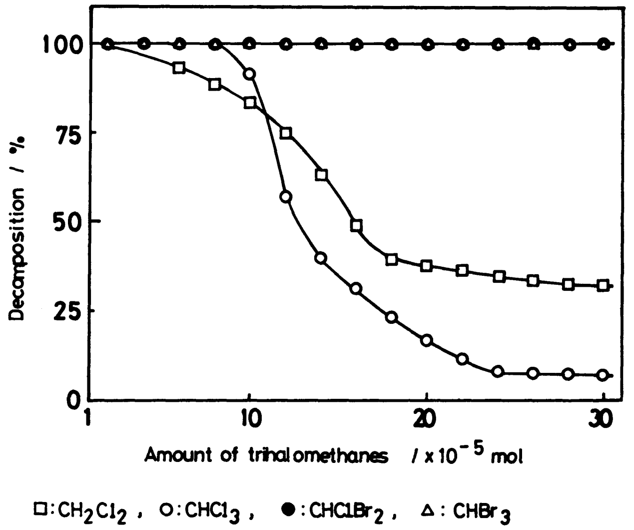

Fig. 2. Effect of the repeated doses of polyhalomethanes on the activity of Fe_3O_4 for the oxidative decomposition producing CO_2 at 623 K.

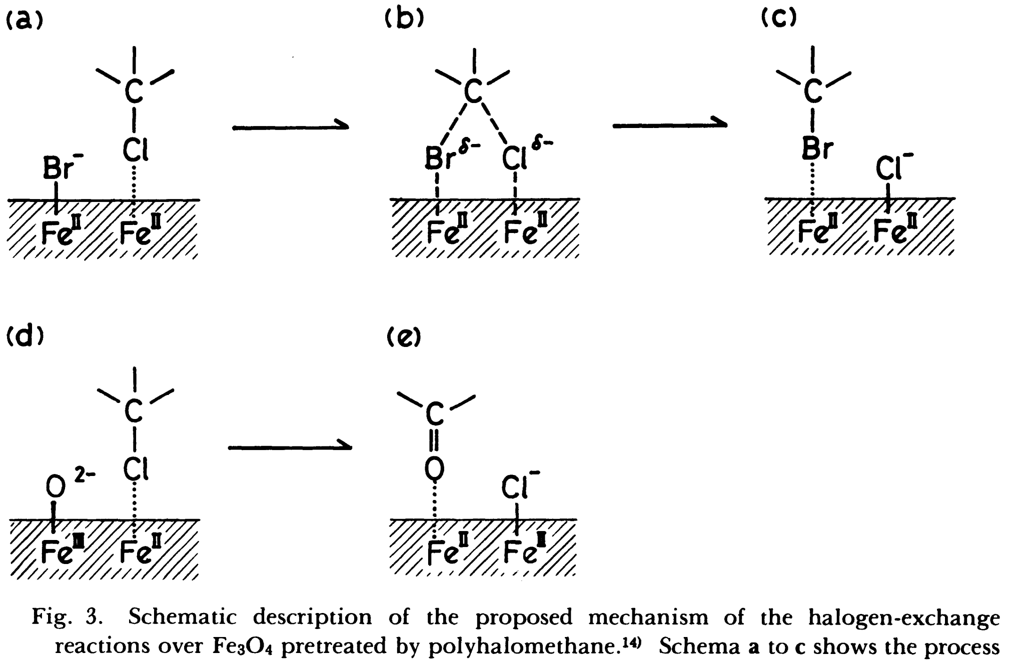

Fig. 3. Schematic description of the proposed mechanism of the halogen-exchange reactions over Fe_3O_4 pretreated by polyhalomethane.[14] Schema **a** to **c** shows the process of replacement of chlorine to bromine on the surface of $CHBr_3$-pretreated Fe_3O_4 catalyst. During the process of pretreatment, oxide ion (O^{2-}) bound to Fe(III) is assumed to be replaced reductively by halide ion as illustrated by schema **d** and **e**.

decomposition after being washed with water.

In a run in which a well-blended and annealed mixture of newly prepared Fe_3O_4 and a small amount of iron(II) chloride was used as catalyst, the oxidative decomposition took place as usual but the halogen exchange did not proceed to a measurable extent. This fact suggests that nonhalogenated iron sites (probably Fe(II)) on the suface of the catalyst should play a critical role in the pathway of the halogen-exchange reaction. The mere contact of polyhalomethane with chloride ion does not seem to induce the exchange of halogen measurably, since the chlorine atoms of chlorinated methanes were shown to exchange very slowly with chloride ion even in a homogeneous liquid phase.[13] On the other hand, neither oxidative decomposition nor halogen exchange proceeds to give considerable amounts of the products when Fe_2O_3 (hematite) was employed instead of Fe_3O_4 as the catalyst. These facts imply that Fe(II) species should play a crucial role in the reaction. By all accounts, Fe(II) species linked to halogen is assumed to behave as a halogen donor and Fe(II) species adjacent to the Fe(II)-halogen linkage to act as a halogen acceptor in the reaction.

A mechanism which involves a bridged transition state (shown in Fig. 3b) might be one of the most probable pathways which explains the exchange reaction. The reaction is supposed to proceed through the following three steps in this mechanism. The mechanism is illustrated by the example of dechlorination–bromination in Fig. 3. (i) In the first step, the chlorine atom of a chlorinated methane molecule (ClCXYZ) forms a coordinative bond to the free iron(II) site located adjacent to the brominated iron(II) species. (ii) A bridged structure like illustrated in Fig. 3b is formed on the surface of the catalyst. Bromide transfer from an Fe(II) site to carbon and chloride transfer from carbon to an adjacent free Fe(II) site proceeds simultaneously through this bridge. (iii) Newly formed brominated methane (BrCXYZ) leaves from the surface. Halogen ligated Fe(II) group on the surface is expected to be

Table 1. Products of the Reactions over Fe_3O_4 Pretreated with $CHBr_3$[a]

Substrate	Reaction temp/K	Reaction product/mol% (Reactant = 100%)							
		CH_2Cl_2	CH_2BrCl	CH_2Br_2	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	CO_2
CH_2Cl_2	393	**98.5**	1.5						
(**1**)	433	**87.5**	12.0						
	473	**62.0**	32.6	4.9					0.5
	513	**34.1**	47.1	17.8					1.0
	553	**25.6**	48.2	23.5					2.7
	593	**21.1**	48.8	24.9					5.2
CH_2BrCl	393		**100.0**						
(**2**)	433		**97.7**	1.2					1.1
	473		**91.8**	6.3					1.9
	513		**78.4**	18.2					3.4
	553		**61.3**	33.1					5.6
	593		**49.2**	44.2					6.6
$CHCl_3$	393				**80.2**	16.2	3.6		
(**3**)	433				**53.6**	32.7	11.3	2.1	0.3
	473				**39.1**	43.4	14.9	2.0	0.6
	513				**28.4**	46.4	15.8	2.1	7.3
	553				**19.4**	32.6	13.3	2.6	32.1
	593				**12.9**	17.5	9.2	3.2	57.2
$CHBrCl_2$	393					**94.7**	5.1		0.2
(**4**)	433					**70.8**	18.9	3.4	6.9
	473					**53.1**	27.5	8.6	10.8
	513					**45.2**	30.1	10.4	14.3
	553					**34.5**	28.2	11.0	26.3
	593					**21.9**	22.7	10.8	44.6
$CHBr_2Cl$	393					0.5	**93.4**	6.1	
(**5**)	433					8.4	**70.9**	20.2	0.5
	473					11.2	**57.9**	29.4	1.5
	513					12.1	**47.6**	36.1	4.2
	553					9.7	**36.8**	35.1	18.4
	593					8.9	**20.2**	25.1	45.8

a) Bold figures in the Tables 1 and 2 represent the percentages of the remaining reactant.

formed by the reductive chlorination–deoxygenation of Fe(III)–O group by a polyhalomethane during the process of pretreatment (as illustrated by the process from (d) to (e) of Fig. 3). The scheme includes a bridged structure which has not been supported by direct experimental evidence and, therefore, is rather speculative. However this explains the overall process of the halogen-exchange reaction if we assume that C–Cl bonds are considerably more difficult to cleave than C–Br bonds. Especially, the fact that the well-blended mixture of Fe_3O_4 and $FeCl_2$ does not activate the exchange reaction supports the participation of the neighboring Fe(II)–Cl and nonligated Fe(II) sites of the surface.

Quantitative Survey on the Halogen-Exchange Reactions. Dichloromethane (**1**), bromochloromethane (**2**), trichloromethane (**3**), bromodichloromethane (**4**), and dibromochloromethane (**5**) were vaporized in the stream of helium at various temperatures and introduced to the reactor filled with fine particles of the Fe_3O_4 catalyst pretreated with bromoform. The products of the pulse reactions are given as a function of temperature in Table 1. The results of the similar reactions of dibromomethane (**6**), **2**, tribromomethane (**7**), and **4** over the Fe_3O_4 catalyst pretreated with chloroform are also shown in Table 2.

Both dechlorination–bromination and debromination–chlorination reactions proceed predominantly in the runs carried out at lower temperatures. Multiple exchange also occurs giving, for example, bromodichloro-, dibromochloro-, and tribromomethanes starting from chloroform. Since the singly exchanged product is the most predominant and the triply exchanged one the least predominant, only one halogen atom must be exchanged by a single contact of the substrate (polyhalomethane) on the surface of the pretreated Fe_3O_4. The halogen atoms are exchanged consecutively, giveing a multiply exchanged product after multiple contacts to the active site of the catalyst. The oxidative decomposition producing carbon dioxide becomes significant in the runs at elevated temperatures. Trihalomethanes are more susceptible to the decomposition, producing carbon dioxide and water as the most predominant product at higher temperatures. In contrasts, dihalomethanes (**1**, **2**, and **6**) produce carbon dioxide only subsidiarily in the range of temperature investigated.

The dechlorination–bromination reactions in Table 1 behave remarkably different from the debromination–chlorination reactions in Table 2 in some respects. The dechlorination–bromination seems to be a kinetically controlled reaction of which rate-determining step is the cleavage of C–Cl bond. The

Table 2. Products of the Reactions over Fe_3O_4 Pretreated with $CHCl_3$ a)

Substrate	Reaction temp/K	Reaction product/mol% (Reactant = 100%)							
		CH_2Cl_2	CH_2BrCl	CH_2Br_2	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$	CO_2
CH_2BrCl (**2**)	393	34.4	**62.5**			3.0			0.1
	433	48.1	**42.1**			8.1			1.7
	473	43.9	**43.1**			10.9			2.1
	513	39.1	**45.3**			12.6			3.0
	553	36.8	**45.2**			12.9			5.1
	593	37.0	**42.4**			6.3			14.3
CH_2Br_2 (**6**)	393	29.5	21.1	**48.4**					
	433	67.2	17.6	**14.8**					0.4
	473	63.2	25.7	**9.7**					1.4
	513	34.5	44.5	**18.8**					2.2
	553	22.1	42.6	**29.5**					5.8
$CHBrCl_2$ (**4**)	393				82.6	**11.2**			6.2
	433				80.8	**11.9**	0.2		7.1
	473				70.7	**13.8**	1.1		14.4
	513				55.2	**18.6**	2.1		24.1
	553				29.9	**17.1**	2.5		50.5
	593				20.1	**8.7**			71.2
$CHBr_3$ (**7**)	393				15.0	27.3	28.1	**16.7**	12.9
	433				11.8	24.4	28.9	**14.3**	20.6
	473				4.8	11.8	23.5	**23.4**	36.5
	513				0.3	2.7	18.4	**38.8**	39.8
	553						16.3	**13.8**	69.9
	593						11.9	**8.2**	78.9

a) See the footnote of Table 1.

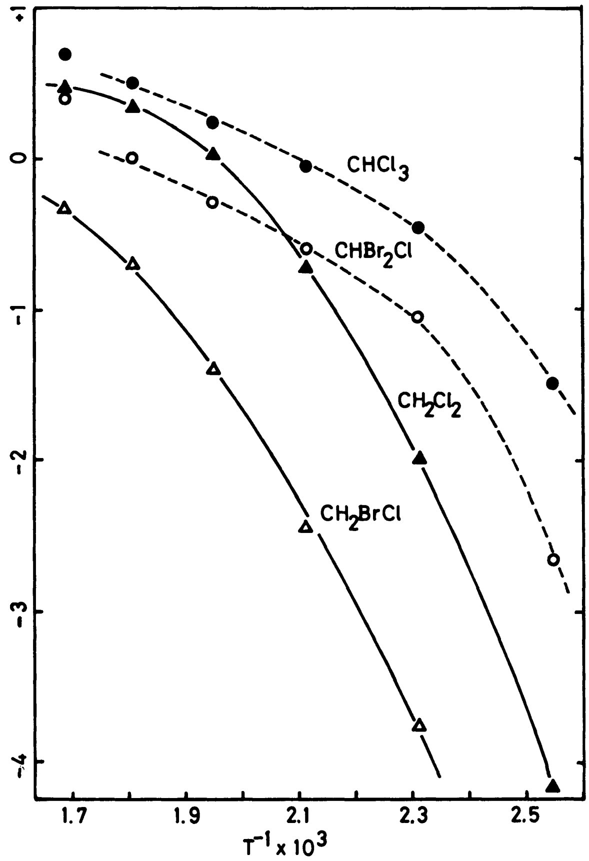

Fig. 4. The Arrhenius plots for the consumption of chlorinated methanes over Fe_3O_4 pretreated by $CHBr_3$.

plots of logarithm of the relative rate[15] (k_{rel}) versus the inverse of reaction temperature ($1/T$), illustrated in Fig. 4, gave the activation energies for the decay of (poly)chloromethanes. The apparent activation energies (E_a) at 427 K for **1**, **2**, **3**, and **5** are 47.2, 54.0, 16.1, and 18.3 kJ mol^{-1}, respectively. The E_a values for trihalomethanes **3** and **5** are considerably lower than those for dihalomethanes **1** and **2**. The lower E_a for trihalomethanes can partly be accounted for the contribution of the steric and electrostatic repulsion among three halogen atoms of trihalomethanes, which facilitates the release of halogen atom.

On the contrary, debromination–chlorination reactions were more complicated. It produced a mixture of a significant amounts of multiply exchanged, further-chlorinated, and oxidized products in addition to the singly exchanged product. The decrease of the starting material was irregularly dependent on the reaction temperature, suggesting that the initial cleavage of C–Br bond is not rate-determining at least at elevated temperatures and that multiple exchange and retro-exchange(dechlorination–bromination) proceed rather extensively. Some bond-forming steps in these secondary processes must determine the rate of the reaction. Since the C–Br bond energy is considerably lower than that of C–Cl bond and, therefore, chlorinated methanes are more stable than the corresponding brominated methanes, the above interpretation is reasonable.

The authors are grateful to Professor S. Fukushi, Chiba Institute of Technology, for his valuable advice and encouragement throughout this work. They also thank heartily to Dr. Tetsuo Ishii, Yokohama Research Institute for Environmental Protection, for his discussion from the view of environmental science and for the measurement of GC/MS spectra.

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12) When polybromomethanes (**6** and **7**) were treated at lower temperatures, the extent of the decomposition was shown to decrease gradually as the amount of dose increased, giving dose vs. percentage of decomposition curves which are similar to those for **1** and **3**.

13) K. Tanabe, *Nippon Kagaku Zasshi,* **87**, 629 (1966) and references cited therein.

14) As triiron tetraoxide (magnetite) is known to be composed of $Fe^{II}Fe^{III}[Fe^{III}O_4]$, one of Fe(III) is coordinated tetrahedrally by four oxide (O^{2-}) ions and located in the neighborhood of a free Fe(II) species in the inverse spinnel type lattice. This arrangement is illustrated schematically in Fig. 3d depicting only one Fe(III)-oxide-ion linkage which is oriented outward from the surface of the catalyst.

15) Relative rate constants (k_{rel}) were estimated from the percentages of residual reactants by assuming the decay of polyhalomethanes to obey the first-order rate law.