Formation of halocarbons in the methane—alkaline halide crystal system under UV radiation

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The possibility of formation of halomethanes upon the photostimulated reaction of halogen-containing minerals with methane was shown. The dynamics of accumulation of chloromethane, dichloromethane, and chloroform in model systems CH_4 —NaCl, CH_4 —sylvinite, and CH_4 —halite was studied experimentally. The kinetic parameters for the formation of methyl chloride were determined.

Key words: alkaline halides; methane; photochemical reaction.

Study of the origin of organic compounds and also characteristic features of their distribution over the Earth surface is important for the understanding of complex physicochemical processes occurring in the atmosphere. The contribution of geological sources to the formation of the organic constituent of the Earth atmosphere has been little studied so far. Meanwhile, it is known that both inorganic and organic compounds are evolved in the processes of degassing of the upper Earth mantle.¹ It has been reported that rocks and minerals contain halogenated organic derivatives.^{2,3} During production and processing of natural raw materials, volatile compounds present in them are removed to the atmosphere. It can be suggested that both the natural degassing of rocks and human activity are the sources of halohydrocarbons (HHC); on the one hand, these compounds act as "hotbed gases," and on the other hand, they are potential destroyers of the ozone layer of the Earth.

Previously,² we have advanced the hypothesis concerning a radiation-stimulated chemical mechanism of formation of HHC in the Earth upon the reaction of methane with halo-containing rocks on exposure to the high-energy y-quanta resulting from radioactive decay of ⁴⁰K, ²³²Th, ²³⁵U, and ²³⁸U. In this study, we verify this hypothesis in relation to methane-alkaline halide systems. The interaction of alkaline halide crystals (AHC) with organic components of sedimantary rocks is possible only upon activation of the halide ions in the crystal lattice, in particular, upon the formation of lattice defects.⁴ The energy of formation of various types of defects in the series NaCl-KCl-NaBr-KBr ranges from 2 to 8 eV, which corresponds to a quantum wavelength of 250-600 nm. Decomposition of natural radioactive isotopes yields species with energies varying from tenths of MeV to several MeV. Therefore, the action of a y-quantum, resulting from a single radioactive decay event, on the AHC-methane system can lead to the formation of 10^2 - 10^4 defects of various types.⁵

It can be expected that irradiation of AHC with UV quanta with an energy of 2-8 eV should also result in the formation of defects that can interact with methane. The purpose of this study is to model the interaction of methane with AHC defects under conditions when these defects are continuously formed under the action of quanta with the minimum required energy.

Experimental

The experiments were carried out in a 25-mm-high cylindrical quartz reactor with a diameter of 50 mm and two leadaway piles on the generatrix. The samples were withdrawn through sealing coupling nuts with silicone gaskets whose inner surface was covered by a perfluorinated polymeric film. A sample was irradiated through the bottom of the reactor made of optical quartz using a low-pressure mercury lamp (with a maximum at 254 nm) placed in a housing with a hole whose diameter was equal to the reactor diameter. According to measurements by luxometer, the luminuous flux at the level of the irradiation object was 7 μ E s⁻¹.

Natural speciments (sylvinite of the Bereznikovskii deposit and Solikamsk halite) and synthetic sodium chloride were used in the experiments.

The minerals were prepared using two procedures. The specimens used without preliminary purification were ground and sieved, and the other specimens were dissolved, the solution was filtered, then the filtrate was concentrated, the dry residue was ground, and fractions <0.25 mm were cut off. Sodium chloride of "high-purity" grade was employed.

Immediately prior to the experiment, all the specimens were annealed in a muffle furnace at ~500 °C under atmospheric pressure in order to remove adsorbed water and organic compounds. Dried natural gas freed from impurities was used in the experiments.

Distilled water was thoroughly purified from possible chloroform impurity by prolonged refluxing; the purity of the

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resulting material was checked by chromatography under conditions that simulated desorption of the reaction products in the experiments with irradiation.

To determine the composition of the products of the photochemical reaction, after irradiation the gas phase in the reactor was displaced by helium into a sorption tube filled with Polysorb-10. GC/MS analysis of the reaction products was carried out on an LKB-2091 instrument after thermal desorption into a capillary column with dinonyl phthalate.

The components of the reaction mixture were analyzed by GC on a 3700 instrument [electron-capture detector, 2 m × 3 mm columns packed with Silipor 600 (0.125-0.160 mm) and Porapack QS (0.16-0.25 mm), column temperature 120 °C]. Quantitative analysis was carried out on a column with Silipor 600. Porapack QS was used to identify the products of the synthesis based on the retention indices.^{7,8} The detector was calibrated against artificial gas mixtures.

A sample was placed in the reactor as a ~1 mm thick bed (-2 g). High-purity nitrogen was passed through the reactor in order to remove atmospheric oxygen and water vapor, and then the reactor was filled with methane. The concentration of the components in the reaction mixture was measured over a period of 3-6 h; five or six 1 mL samples were analyzed every 30-50 min. Some of the experiments ended with desorption of the reaction products, which were washed from the AHC surface with 2 mL of distilled water. With allowance for the distribution ratio, the salting-out effect, and the ratio of the two phases (gas and liquid), more than 90% of the HHC adsorbed initially on the AHC surface passed to the gas phase; the gas phase was then analyzed by chromatography.

Results and Discussion

The following compounds were identified in the product mixture formed upon the photochemical reaction: MeCl, CH₂Cl₂, CHCl₃, EtCl, PrCl, MeBr, EtBr, and MeCl (the major component). The presence of a relatively large amount of EtCl is due either to incomplete removal of the impurities of homologues from methane or, what is more likely, to the occurrence of the following processes typical of methane:

$$CH_4 + hv \longrightarrow CH_3' + H'$$

2 $CH_3' \longrightarrow C_2H_6.$

The presence of PrCl and EtBr among the reaction products is apparently due to the same reasons. The formation of alkyl bromides can be explained by the presence of bromide impurities in chloride minerals. According to ionic chromatography, the average content of Br^- in sylvinite amounts to ~0.1%.

The content of polychlorinated halomethanes (CH₂Cl₂, CHCl₃) is relatively low, while CCl₄ was not detected at all.

To estimate the content of HHC in the initial chlorides, blank experiments were carried out. The specimens prepared for photochemical experiments were irradiated under inert atmosphere until the highest HHC concentration in the gas phase was attained. Then the components were desorbed by distilled water. The results of the blank experiments are listed in Table 1. The presence of slight Table 1. Content of hydrocarbons (µg L⁻¹) over various AHC determined in blank experiments

Halide	MeCl	CH ₂ Cl ₂	CHCl3
Purified sylvinite	1.2	0.00	0.00
Crude sylvinite	1.5	0.05	0.00
Purified halite	0.5	0.02	0.00
Crude halite	0.9	0.06	0.03
NaCl	0.2	0.06	0.05

Note. Here and in Tables 2-4, irradiation was carried out with a mercury lamp ($\lambda = 254$ nm, intensity 7 μ E m⁻² s⁻¹) in a N₂ atmosphere.

amounts of HHC on the surface of minerals and NaCl after heating at ~500 °C is apparently due to the incomplete opening of gas occlusions in crude minerals.

Dark desorption of HHC from salts prepared for the experiment was also studied. Only purified specimens (NaCl, halite, and sylvinite) were used in these experiments, because dissolution could result in the removal of the HHC occurring in occlusions.

Decomposition of HHC on AHC under the action of UV radiation was carried out by introducing a model gas mixture, in which the concentrations of HHC corresponded to the linear dynamic range of the electroncapture detector, in the reactor filled with nitrogen and an AHC. Preliminarily, a weighed portion of an AHC was placed in the reactor and purged with nitrogen. The experiment lasted for 2-5 h depending on the rate of decomposition of HHC. These experiments were carried out in order to elucidate the possibility of a photocatalytic mechanism of formation of HHC according to the following scheme:

2 CH₃Cl \rightarrow CH₄ + CH₂Cl₂.

The results of these studies are presented in Table 2.

In none of the studied systems was the fast decomposition of the initial HHC accompanied by accumulation of any halomethane. In order to confirm the surface character of the process, photochemical decomposition of individual HHC in the gas phase in the absence of a salt was studied; this made it possible to elucidate the possibility of mutual transformations of halomethanes under the action of UV radiation (Table 3).

The data presented in Table 3 demonstrate that no noticeable mutual transformations of halomethanes occur in the gas phase. In addition, the rate of photoinduced gas-phase decomposition increases in the series $MeCl < CH_2Cl_2 < CHCl_3$. The rate of decomposition of individual halomethanes on the surface of an AHC increases in the same sequence.

The data on the rate of accumulation of HHC are given in Table 4. These data demonstrate that in all of the systems without exception, chloromethane is formed as the major product; its concentration increases with time and reaches a steady-state value. Dichloromethane and chloroform are not accumulated in the gas phase.

Apparently, they are formed by a more complex mechanism than successive chlorination of methane $CH_4 \rightarrow CH_3Cl \rightarrow CH_2Cl_2 \rightarrow CHCl_3 \rightarrow CCl_4$.

 Table 2. Kinetics of the photostimulated decomposition of HHC on the AHC surface

Halide	t	MeCl	CH ₂ Cl ₂	CHCl3
	/min		µg L ^{−1}	
Purified	0	8.2	3.1	2.8
sylvinite	30	11.0	2.9	1.7
	50	9.3	2.1	0.86
	70	8.1	1.7	0.69
	90	7.7	1.5	0.50
	110	7.9	1.4	0.39
Crude	0	18.0	5.2	1.9
sylvinite	30	18.0	5.2	1.7
	50	19.0	4.5	1.4
	70	15.0	2.6	0.72
	90	4.2	0.4	0.11
Purified	0	9.7	4.8	2.4
halite	30	7.6	3.3	l <i>.</i> 4
	60	4.7	1.5	0.43
	80	4.0	1.3	0.39
	100	4.4	1.2	0.26
	120	4.3	0.93	0.17
	150	2.4	0.42	0.07
Crude	0	9.7	7.6	7.2
halite	30	9.7	3.7	2.2
	50	14.0	4.5	1.4
	70	7.5	1.6	0.36
	90	5.2	0.87	0.15
	110	4.0	0.58	0.10
NaCl	0	9.2	3.6	2.2
	30	8.9	2.8	1.1
	60	7.0	1.6	0.50
	80	4.6	0.78	0.24
	100	5.1	0.69	0.21
	120	2.5	0.32	0.11
	140	1.8	0.25	0.09

Note. Determination errors (%): MeCl 12.0, CH_2Cl_2 19.0, $CHCl_3$ 14.0.

 Table 3. Kinetics of the photostimulated decomposition of HHC in the gas phase without AHC

Hydrocarbon	t	MeCl	CH ₂ Cl ₂	CHCl3
	/min		μg L ⁻¹	
CH ₃ Cl	0 20	44.8 0.1	0.71 0.08	0.02
CH ₂ Cl ₂	0 20 75	0.3	12.89 5.71 0.47	0.01 0.01 0.01
CHCl3	0 20		0.21 0.33	5.93 0.07

Note. Determination errors (%): MeCl 12.0, CH_2Cl_2 19.0, $CHCl_3$ 14.0

* The concentration of the component was below the detection limit. In some experiments on the chlorination of methane, desorption of components fixed on the AHC surface was studied. These studies were necessary to estimate the proportion of components (α) occurring in the gas phase. The results of these experiments (Table 5) demonstrate that up to 90% of the HHC formed upon the photochemical reaction can remain on the AHC surface.

To determine the kinetic parameters, we proposed a model for the process of formation of chloromethane, which is based on the following assumptions.

1. The reaction occurs on the AHC surface.

2. The rate of formation of chloromethane obeys the equation

$$v_0 = k \cdot [CH_4] \cdot I \cdot S_{AHC},$$

where k is the rate constant for the formation of CH_3CI , [CH_4] is the methane concentration in the reactor, *I* is the intensity of the incident radiation, and S_{AHC} is the

 Table 4. Kinetics of accumulation of HHC in the methane-

 AHC--UV-radiation system

Halide	t	MeC1	CH ₂ Cl ₂	CHCl3
	/min		μg L ⁻¹	
Purified	0	*	0.06	_
sylvinite	60	3.9		-
	120	3.0	0.03	
	180	6.7	0.06	0.02
	240	19		0.05
	300	14		0.03
Crude	0	0.1		
sylvinite	30	1.3		0.01
	90	3.8		0.09
	150	6.1		0.01
	210	7.8	****	0.01
	270	8.9		
	330	11	-	0.02
Purified	0		-	
halite	60	2.5		
	120	2.3	0.04	
	180	5.5	-	-
	240	8.5		
	300	10		—
Crude	0	0.3	0.08	0.02
halite	30	2.2	0.03	0.02
	60	4.1	0.02	0.02
	120	4.0	0.02	0.01
	210	7.9	0.01	0.01
	300	12	0.01	0.01
NaCl	0	0.1		0.05
	15	3.0	0.05	0.07
	60	11	0.20	0.11
	135	20	0.22	0.06
	195	19	0.16	0.02

Note. Determination errors (%): MeCl 12, CH_2Cl_2 19, $CHCl_3$ 14. * The concentration of the component was below the detection limit.

Table 5. Parameters α for various hydrocarbons formed from methane

Halide		α	
	MeCl	CH ₂ Cl ₂	CHCl ₃
Sylvinite	0.70	0.24	0.82
Halide	0.96	0.73	0.31
NaCl	0.99	0.17	0.38

Note. Irradiation was carried out with a mercury lamp, $\lambda = 254$ nm with an intensity of 7 $\mu E m^{-2} s^{-1}$ in a CH₄ atmosphere.

surface area of the AHC. It is assumed that all the terms in this equation remain constant under the experimental conditions.

3. An adsorption equation is established on the AHC surface, and the ratio of the amount of CH_3Cl in the gas phase to the total amount of the component formed during the process (α) remains constant.

4. The process is described by the following kinetic equation:

$$\frac{\mathrm{d}M_1}{\mathrm{d}t} = v_0 - k_1 \alpha_1 M_1(t), \qquad (1)$$

where $M_1(t)$ is the amount of CH₃Cl at the time instant t; k_1 is the rate constant for decomposition of CH₃Cl; and α_1 is the proportion of CH₃Cl sorbed on the AHC surface.

In the final form, this equation can be written as follows

$$M_1(t) = \frac{v_0}{k_1 \alpha_1} \left(1 - e^{-k_1 \alpha_1 t} \right).$$
 (2)

The kinetic parameters of the process calculated using this model are listed in Table 6. It can be seen that the rate of formation of CH_3Cl in this system does not depend on the type of AHC used. Conversely, the rate constant for decomposition depends on the type of object: for purified minerals, it is substantially lower than for nonpurified ones. This is due most likely to the fact that nonpurified materials contain photochemically active transition metal compounds as impurities.

Within the framework of this model, time dependences of the amounts of CH_2Cl_2 and $CHCl_3$ were obtained; however, the theoretical curves based on these dependences do not coincide with experimental data, because the dynamics of accumulation of the abovementioned components is more complex than follows from the proposed model. The subsequent development of the model should occur apparently along three lines. Table 6. Kinetic parameters of the equation describing the formation of CH_3Cl during photochemical synthesis on the AHC surface

Halide	ν ₀ /μg L ⁻¹ min ⁻¹	k ₁ · 10 ⁴ /min ⁻¹	
Purified sylvinite	0.047	0.56	
Crude sylvinite	0.049	29.0	
Purified halite	0.033	0.59	
Crude halite	0.064	42.0	
NaCl	0.230	71.0	

1. It is necessary to verify the assumption that the ratios of distribution (α) of halomethanes between the gas and solid phases remain constant during the process.

2. It is necessary to assume that the rate constants for the formation of CH_2Cl_2 and $CHCl_3$ remain constant during the experiment.

3. It is expedient to study the influence of the intensity of irradiation of an AHC sample on the reaction rate.

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