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Kinetics of Methyl Iodide Tribosorption on the Solid-Phase Salt KI

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Abstract—It was found that the tribosorption of methyl iodide from the gas phase of a closed reactor onto a matrix of KI is described by the rate equation for a reversible first-order reaction $v_g - v_{\infty,\,g} = m\,v^*_{ts}\exp(-\eta_{td}D_{sp})$, where v_g and $v_{\infty,\,g}$ are, respectively, the current and equilibrium amounts of methyl iodide in the gas phase; v^*_{ts} is the equilibrium amount of methyl iodide tribosorbed per gram of salt; m is the mass of potassium iodide; η_{td} is a constant, which characterizes the efficiency of tribodesorption ($\eta_{td} = 0.011 \pm 0.005$ g/J); and D_{sp} is the specific dose of mechanical energy absorbed by the KI powder. The value of v^*_{ts} monotonically increased with increasing equilibrium partial pressure of methyl iodide and reached a maximum value of ≈25 μmol/g. The lower limit of the constant η_{td}, which characterizes the efficiency of tribosorption, was estimated at 0.1 g/J.

INTRODUCTION

It is well known that mechanical effects on solids in the gas–solid system are accompanied by tribosorption, the increase of gas sorption by a solid substance [1]. The tribosorption of gases is usually higher than the amount of a gas adsorbed on the surface by one order of magnitude. In the inert gas–metal (Ar/Ni) system, the process is characterized by a constant rate of absorption from the gas phase over a very long time interval of mechanical treatment, except for a short nonlinear initial portion and a portion on turning to saturation, when a thermal desorption equilibrium between gas and solid phases is established [1]. In this state, the linear dependence of the amount of tribosorbed gas on equilibrium gas pressure was obtained for the above system.

We observed tribosorption in the course of the reactions of substitution for the halogen in alkyl iodides in the presence of RI vapors (R = Me, Et, and *n*-Pr) and solid salts MX (MX = NaCl, KCl, CsCl, and KBr); these reactions were activated by continuous mechanical treatment at room temperature [2]. Thus, in the MeI_g–KCl_s system, the release of the reaction product MeCl into the gas phase also continued after almost complete absorption of MeI. Evidently, the kinetics of MeI tribodesorption as an independent phenomenon should be considered in more detail in order to determine the kinetics of tribochemical reactions of MeI with KCl_s. For this purpose, the MeI_g–KI_s system, which is simple and convenient, was used. In this system, MeI did not undergo chemical transformations, and the substrate consumption from a gas phase, which was found previously [2], was due only to tribosorption.

The aim of this work was to study the kinetics of tribosorption of methyl iodide in the course of the continuous mechanical treatment of KI_s powder in a vibrating mill.

EXPERIMENTAL

The weighed portions of the KI salt (m = 0.5 g) were pretreated in a closed steel reactor using an MMVE-0.005 vibrating mill with the power density I = 340 W/kg for 30 min as described elsewhere [2].

The consumption of methyl iodide from the gas phase of the reactor was monitored by GLC. An LKhM-8MD chromatograph with a flame-ionization detector and a 3-m column packed with 5% SE-30 as a stationary phase on Chromaton N AW was used. The partial pressure of methyl iodide was determined by the procedure described previously [3].

The specific surface area of the salt was determined by the BET method from the desorption of argon.

RESULTS AND DISCUSSION

To exclude complications due to an increase in the surface area on milling, the kinetics of tribosorption was studied with a mechanically pretreated powder of KI after reaching the limiting specific surface area S^*_{sp} = 0.55 m^2/g.

Figure 1 demonstrates the typical dependence of the sorption of methyl iodide vapor by the KI salt from the

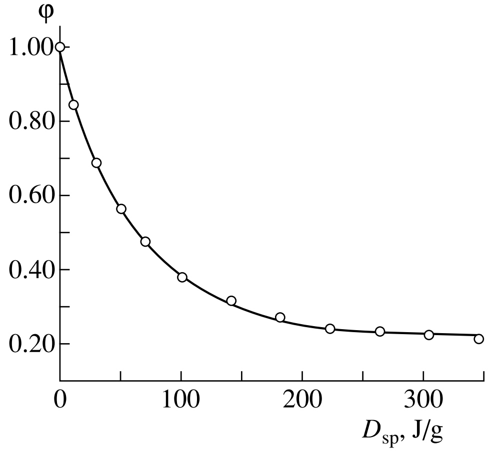

Fig. 1. Dependence of the tribosorption of MeI from the gas phase of the closed reactor on the specific absorbed dose of mechanical energy (D_{sp}).

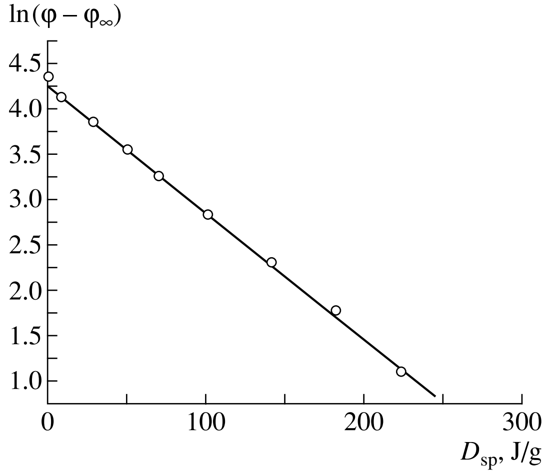

Fig. 2. Dependence of $\ln(\varphi - \varphi_\infty)$ on the specific absorbed dose of mechanical energy in the course of MeI tribosorption from the gas phase.

gas phase of a vibrating reactor on the specific dose (S^*_{sp}) of absorbed mechanical energy (D_{sp}). The relative concentration of methyl iodide in the gas phase of the reactor is $\varphi = P(\mathrm{MeI})/P_0(\mathrm{MeI})$, where P_0(MeI) and P(MeI) are the initial and current partial pressures of methyl iodide in the gas phase of the vibrating reactor, respectively. It can be seen in Fig. 1 that, as distinct from published data [1], φ nonlinearly decreased with time and reached a limiting value of φ_∞. Evidently, this character of the dependence of φ on the absorbed dose of mechanical energy is a consequence of the reversible binding of methyl iodide. Correspondingly, the value of φ_∞ can be considered as the relative concentration of MeI in the gas phase in a state of tribosorption equilibrium. Indeed, the typical $\ln(\varphi - \varphi_\infty)$–$D_{sp}$ relationship corresponds to a first-order rate equation for a reversible process (Fig. 2).

Dependence of the constant that characterizes the rate of MeI absorption from the gas phase of a reactor (η_{expt})and the equilibrium amount of methyl iodide tribosorbed per gram of the salt (v^*_{ts}) on the initial and equilibrium partial pressures of methyl iodide

P_0 (MeI), Pa	P_∞ (MeI), Pa	v^*_{ts}, µmol/g	$\eta_{expt} \times 10^2$, g/J
325	47.3	2.80	1.26 ± 0.09
627	158	4.72	0.97 ± 0.03
1419	165	12.62	1.83 ± 0.07
2038	432	16.20	1.43 ± 0.02
2807	615	22.04	0.83 ± 0.02
3376	1262	21.26	1.53 ± 0.06
3961	1389	25.88	0.83 ± 0.02
4422	1881	25.56	0.83 ± 0.02
Average value			1.1 ± 0.5*

The table summarizes the experimental constants $\eta_{expt} = -d(\ln(\varphi - \varphi_\infty))/dD_{sp}$, which characterize the rate of MeI absorption, depending on the initial partial pressure P_0(MeI) of the substrate in the gas phase. The above values are independent of P_0(MeI) within the limit of experimental error. The amount of methyl iodide tribosorbed per gram of the KI salt in a tribosorption equilibrium (v^*_{ts}) as a function of the equilibrium pressure P_∞(MeI) appears as a saturation curve (table; Fig. 3).

It is well known that the rate of tribosorption and the amount of a tribosorbate depend on the concentration $[\mathrm{MeI}]_{ads}$ of gas molecules adsorbed on the surface of a solid substance from a gas phase [1]. In this context, the tribosorption of MeI on KI can be schematically represented in the following form:

$$\mathrm{MeI_g} \longleftrightarrow \mathrm{MeI_{ads}} \longleftrightarrow \mathrm{MeI_{ts}}, \qquad \text{(I)}$$

where $\mathrm{MeI_g}$, $\mathrm{MeI_{ads}}$, or $\mathrm{MeI_{ts}}$ is methyl iodide in the gas phase of the reactor, adsorbed on the surface of KI, or tribosorbed into the KI matrix, respectively.

In accordance with scheme (I), we write the following equation for a material balance on methyl iodide:

$$v = v_g + [\mathrm{MeI}]_{ads} S^*_{sp} m + v_{ts} m, \qquad (1)$$

where ν_g is the number of moles of methyl iodide in the gas phase of the reactor; ν_{ts} is the specific amount of tribosorbed methyl iodide (the amount of methyl iodide tribosorbed per gram of the salt); and ν is the total amount of methyl iodide.

The adsorption of methyl iodide on the preactivated surface of the KI salt was insignificant over a wide range of partial pressures P_0(MeI). In contrast to adsorption on the surface of the preactivated KI salt, we failed to determine the surface concentration $[\mathrm{MeI}]_{ads}$ of adsorbed methyl iodide using the method described previously [3]. This allowed us to ignore the term $[\mathrm{MeI}]_{ads}S^*_{sp}m$ in Eq. (1). Taking into consideration this circumstance, upon differentiating Eq. (1) with respect to time, we obtain

$$\frac{d\nu_g}{dt} + m\frac{d\nu_{ts}}{dt} \approx 0. \quad (2)$$

In terms of scheme (I), the change in the amount of tribosorbed methyl iodide with time is described by the equation

$$m\frac{d\nu_{ts}}{dt} = k_{ts}[\mathrm{MeI}]_{ads}S^*_{sp}m - k_{td}(\nu_0 - \nu_g), \quad (3)$$

where k_{ts} and k_{td} are the rate constants of tribosorption and tribodesorption, respectively, and ν_0 is the amount of methyl iodide introduced into the reactor. Upon substituting Eq. (3) into Eq. (2) and integrating with consideration for the initial condition $\nu_g = \nu_0$ at $t = 0$, we obtain

$$(\nu_g - \nu_{\infty,\,g}) = \frac{[\mathrm{MeI}]_{ads}S^*_{sp}mk_{ts}}{k_{td}}\exp(-k_{td}t), \quad (4)$$

where $\nu_{\infty,\,g}$ is the amount of methyl iodide in the gas phase after the attainment of a tribosorption equilibrium. Finally, changing from the time of treatment to the specific dose of absorbed energy $D_{sp} = It$, we obtain the final equation

$$\nu_0(\varphi - \varphi_\infty) = \frac{[\mathrm{MeI}]_{ads}S^*_{sp}m\eta_{ts}}{\eta_{td}}\exp(-\eta_{td}D_{sp}), \quad (5)$$

where η_{ts} and η_{td} are the constants that characterize the efficiency of tribosorption and tribodesorption, respectively.

Equation (5) adequately describes experimental data at $\eta_{expt} = \eta_{td}$ (Fig. 2; table). It follows from Eq. (5) that the limiting specific amount of tribosorbed methyl iodide is

$$\nu^*_{ts} = \frac{[\mathrm{MeI}]_{ads}S^*_{sp}\eta_{ts}}{\eta_{td}}. \quad (6)$$

Substitution of an equation of the Langmuir adsorption isotherm for MeI allowed us to obtain the following equation, which describes the run of the saturation curve of ν^*_{ts} as a function of P_∞(MeI) (Fig. 3):

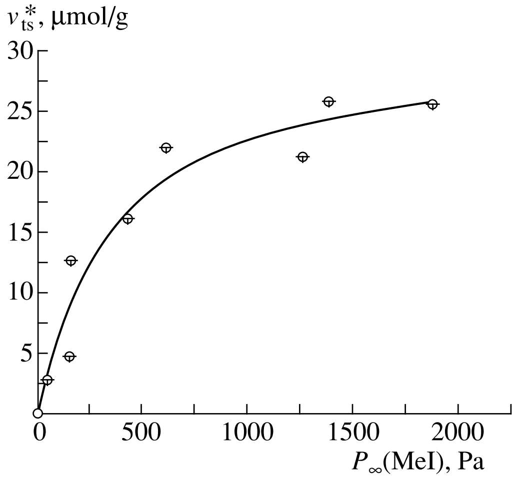

Fig. 3. Dependence of the equilibrium amount of methyl iodide tribosorbed per gram of the salt (ν^*_{ts}) on the equilibrium partial pressure of methyl iodide. Points correspond to experimental values, and the curve was calculated using Eq. (7) at $[\mathrm{MeI}]_{max} = \frac{S^*_{sp}\eta_{ts}}{\eta_{td}} = 31 \pm 3$ μmol/g and $K_{ads} = 2.6 \pm 0.9\ \mathrm{Pa}^{-1}$.

$$\nu^*_{ts} = \frac{[\mathrm{MeI}]_{max}K_{ads}P_\infty(\mathrm{MeI})}{1 + K_{ads}P_\infty(\mathrm{MeI})}\frac{S^*_{sp}\eta_{ts}}{\eta_{td}}, \quad (7)$$

where K_{ads} is the adsorption equilibrium constant, and $[\mathrm{MeI}]_{max}$ is the maximum surface concentration of methyl iodide in the adsorption monolayer. Equation (7) is consistent with experimental data at $K_{ads} = (2.6 \pm 0.9) \times 10^{-3}\ \mathrm{Pa}^{-1}$ (Fig. 3). The resulting adsorption equilibrium constant of methyl iodide on the surface of KI is close to the corresponding value for methyl iodide adsorption on the surface of KCl, $K_{ads} = (0.9 \pm 0.2) \times 10^{-3}\ \mathrm{Pa}^{-1}$ [3]. It is evident that the fulfillment of the Langmuir equation for methyl iodide adsorption implies that adsorption occurs at any surface site rather than only at surface defects.

The experimental data allowed us to estimate the constant η_{ts}, which characterizes the efficiency of methyl iodide tribosorption. Taking into account that the tribosorption of gases is usually greater than the amount of the gas adsorbed on the surface by one order of magnitude [1], we have $\eta_{ts}/\eta_{td} \geq 10$. Thus, we obtain the lower limit of η_{ts}: $\eta_{ts} \geq 0.1$ g/J. With the use of this value, we can estimate the upper limit of the maximum surface concentration of methyl iodide in the adsorption monolayer from data given in Fig. 3: $[\mathrm{MeI}]_{max} \leq 5.6 \pm 0.6$ μmol/m^2.

In conclusion, we consider a plausible mechanism of the mechanochemical process studied. Mechanochemical treatment at a constant specific surface area of a solid salt implies that the rate of formation of a new surface (particle splitting) is equal to the rate of decay of the existing surface (molecularly dense aggregation of particles). It is likely that a solid solution of methyl iodide in a KI matrix is the product of tribosorption. It would be assumed that methyl iodide was also included in the inner cavities of a solid phase, which are isolated from the outer gas phase. However, this pathway does not significantly contribute to tribosorption: in this case, in contrast to experimental data, the limiting specific amount of tribosorbed methyl iodide v_{ts}^{*} would be proportional to the partial pressure of methyl iodide rather than to its surface concentration $[\mathrm{MeI}]_{\mathrm{ads}}$.

The kinetics of tribochemical reactions of gaseous methyl iodide with the solid-phase salt KCl under continuous mechanical treatment will be considered in subsequent communications.

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