The Reactions of Tetrachloride Germanium with Atomic Hydrogen and Chlorine

M. S. Galkin* and S. V. Zelentsov

Department of Chemistry, University of Nizhni Novgorod, Russia

*Author for correspondence e-mail: free_cool@mail.ru

The main sources of high-purity germanium in micro- and optoelectronics are GeH_4 and its derivatives, $GeH_{(4-n)}Cl_n$ (n = 0-4). Existing methods for the chemical synthesis of these substances lead to contamination of the final product by impurities which are difficult to remove. Therefore, it is very important to develop new methods for obtaining these compounds. One of such methods is radical reactions of germanium chloride (IV) with the atomic hydrogen and/or chlorine.

$$GeH_{(4-n)}Cl_n + H\cdot \rightleftarrows GeH_{(4-n)}Cl_{(n-1)}\cdot + HCl \quad (1)$$

$$GeH_{(4-n)}Cl_n + Cl\cdot \rightleftarrows GeH_{(4-n)}Cl_{(n-1)}\cdot + Cl_2 \quad (2)$$

$$GeH_{(4-n)}Cl_{(n-1)}\cdot + H\cdot \rightleftarrows GeH_{(5-n)}Cl_{(n-1)},\ n=1-4 \quad (3)$$

Reaction mechanism of $GeCl_4$ with H and Cl has been studied using modern quantum chemical methods UQCISD (FC)/6-311+G(3df,2pd), UMP2 (FC)/6-311+G(d,p) and UB3LYP/6-311+G(d,p). For every step of these reactions there have been calculated potential barriers ($\Delta E_{forward}$ and $\Delta E_{backward}$), the enthalpies of reactions ($\Delta_r H^0$, p = 0.1013 MPa, T = 298 K, the gas phase) and bond dissociation energies (E_b (Ge-Cl)) (Tables 1,2).

Table 1

Reaction	$\Delta_r H^o$,[1] kcal·mol^{-1}	ΔE, kcal·mol^{-1}		E_b, kcal·mol^{-1}
		Forward	Backward	
$GeCl_4 + {}^{\cdot}H$	-9.8	12.05	23.55	92.12
$GeCl_3H + {}^{\cdot}H$	-7.2	13.30	21.00	93.56
$GeCl_2H_2 + {}^{\cdot}H$	-5.6	14.37	20.93	95.16
$GeClH_3 + {}^{\cdot}H$	-2.4	14.10	21.42	95.01

Table 2

Reaction	$\Delta_r H^o$,[1] kcal·mol^{-1}	ΔE, kcal·mol^{-1}	
		Forward	Backward
$GeCl_4 + {}^{\cdot}Cl$	35.4	63.84	30.85
$GeCl_3H + {}^{\cdot}Cl$	38.0	68.34	29.10
$GeCl_2H_2 + {}^{\cdot}Cl$	39.6	70.20	25.89
$GeClH_3 + {}^{\cdot}Cl$	42.8	72.52	27.95

$\Delta E_{forward}$ of the reactions of $GeH_{(4-n)}Cl_n$ (n = 1 - 4) with Cl are very high therefore it is unlikely that Cl can take part in the destruction of bond Ge-Cl. Comparatively low stability of $GeCl_2H_2$, $GeClH_3$, and small $\Delta E_{forward}$ to break bond Ge - H under the action of hydrogen (about 3.16 kcal·mol^{-1} [2]) or chlorine (less than 0.5 kcal·mol^{-1}) we may conclude that the practical interest for chemical manufacture is only the reaction $GeCl_4 + {}^{\cdot}H \rightleftarrows GeCl_3\cdot + HCl$. Hence, the main product of the $GeCl_4$ reaction with hydrogen, excluding the influence of the solid surface at a relatively low temperature is $GeHCl_3$. These conclusions are in agreement with the results of the experiments [3,4].

References

1. R. D. Pablo and J .C. Carlos, Journal of Physical Chemistry A, 2008, 112, 6198-6204.
2. Q. Zhang, Y. Gu and S. Wang, Journal of Physical Chemistry A, 2003, 107, 3884-3890.
3. T. Yasuo and I. Hiromu, Journal of Electrochemical Society, 1988, 135, 1539-1543.

K. J. Miller and M. J. Grieco, Journal of Electrochemical Society, 1964, 111, 1099-1101.