Role of Ionic Defects in Photolysis of Lithium Hydride

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Kinetic parameters of photoconductivity and dark conductivity of lithium hydride under uv irradiation have been investigated. A kinetic scheme of lithium hydride photolysis is suggested. Kinetic features of hydrogen evolution under uv irradiation of lithium hydride are explained. The contributions of radiation induced defects and equilibrium cation vacancies to processes leading to gas evolution under photolysis are determined.

Introduction

Directed regulation of the reactivity of solids becomes possible if one takes into account the participation of defects in a chemical reaction (*1*). Lithium hydride provides a good model system for these investigations. This compound is well studied and is similar to alkali–halide crystals (*2, 3*). However, there are substantial differences in the properties of electron excitations, the manner of their autolocalization (*4, 5*), and probably in the decomposition mechanism (*6*).

The main goal of this work was the elucidation of the role of ionic defects of LiH in its photochemical decomposition (PCD). Our approach consists in direct experimental investigation of ionic defects in the course of LiH PCD. One must also follow the electron processes and evolution of the gaseous product of PCD hydrogen, the regularities of the latter process being yet unstudied. It is then possible to construct a kinetic scheme of the processes leading to gas evolution during irradiation. PCD is considered here as a complex ion–electron process, the radiative formation of defects during the decomposition of an autolocalized exciton being taken into account (*6, 7*).

Experimental

LiH samples were cleaved in argon from monocrystals synthesized according to (*8, 9*). The ionic conductivity of LiH due to the motion of cation vacancies (*2, 3, 10*) has been investigated by a standard technique (*11*). Ultraviolet (uv) irradiation by 4–7 eV quanta stimulates in LiH hole type photoconductivity (*12*). As the adsorption coefficient of LiH is rather large in the region 2400–2600 Å ($K = 10^5$ cm^{-1} (*13*)), a cell of the surface type has been used to study the kinetics of the photocurrent. Measurements were performed in the region of voltage where ohmicity of silver contacts was maintained. To study the kinetics of gas evolution during uv irradiation of LiH, a

device in the dynamical regime (regime of continuous pumping out) has been used with an omegatron type transducer IPDO-I which allowed the detection of the rate of the gas evolution from a sample for each component separately (14). The rate of evolution is given by the expression

$$V(t) = \frac{F}{V}(P_2(t) - P_1) + \frac{dP_2}{dt}, \quad (1)$$

where P_1 is the partial pressure of a gas in the system, $P_2(t)$ is the pressure of the given gas at time t after beginning the irradiation, F is the vacuum line conductance, V is the volume of the vacuum system. For our installation $F/V \sim 1$ sec^{-1}, the variation of partial pressure during PCD occurs in several minutes, so that the second term in the above expression is small and can be neglected. The number of gas molecules evolved during one second is determined (14, 15) as

$$\frac{dN}{dt} = \frac{F\Delta P}{kT} = 9.6 \times 10^{18} \frac{F\Delta P}{T}, \quad (2)$$

where $\Delta P = P_2(t) - P_1$. The residual vacuum in the system is $P_1 = 1.15 \cdot 10^{-5}$ Pa. A mercury lamp SVD-120 a served as a source of radiation. Separate spectral bands have been selected by a set of interference light filters UVKSIF.

Results

Gas evolution during PCD of LiH has not been studied previously. It is known that during irradiation of LiH samples only hydrogen is evolved in the gaseous phase. When irradiation is initiated, the hydrogen pressure in the system starts to grow with a delay of 15–100 sec, depending on the uv light intensity; it reaches its maximum and then decreases to a stationary value (Fig. 1a). Switching off the uv light results in a decrease of the gas evolution rate ν_{H_2} which persists about 4–5 minutes (Fig. 1b). During
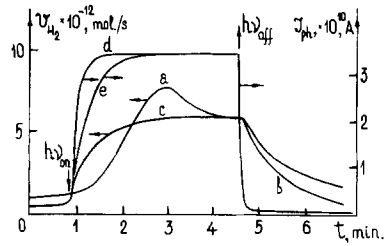

FIG. 1. Kinetics of hydrogen evolution and photocurrent kinetics during uv irradiation of LiH: (a, b, e) non-irradiated sample; (c, d) irradiated sample.

the subsequent irradiations of a once-irradiated sample, the kinetics of gas evolution during photolysis change: the maximum disappears and one observes a slower decrease of hydrogen pressure to the stationary value (Fig. 1c). The fall of the gas evolution rate after switching off the uv light becomes more rapid. Experiments showed that an increase of the uv irradiation intensity leads to a maximum in the kinetic curve $\nu_{H_2}(t)$. Short time annealing of a sample at a temperature 350–370 K produces similar results.

The kinetics of the hydrogen pressure decrease after switching off uv light is described by the hyperbolic dependence $\nu(t) = \nu_0/(t/\tau + 1)^\alpha$, where $\nu(t)$ is the gas evolution rate at time t, ν_0 is the stationary gas evolution rate at time $t = 0$, when uv light is switched off, $\tau \sim 50 \pm 10$ sec, $\alpha = 1$ at initial stages of photolysis, $\alpha = 2$ at the samples which were strongly illuminated
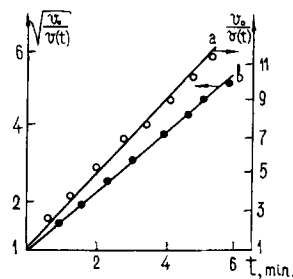

FIG. 2. Kinetics of the hydrogen pressure fall after LiH irradiation is switched off: (a) initial states of PCD; (b) strongly illuminate sample.
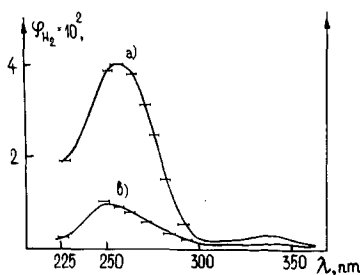
FIG. 3. Spectral dependence of the quantum output of LiH photolysis: (a) initial stages of PCD; (b) deep photolysis.
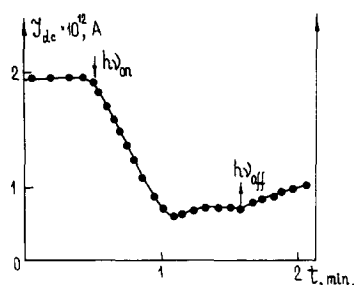

FIG. 4. Variation of the dark conductivity (dc) of LiH during uv irradiation.

(Fig. 2). The spectral dependence of the stationary gas evolution rate during photolysis is shown in Fig. 3a. The maximum of the curve corresponds to the edge of the fundamental absorption (13). Calculations showed that the quantum yield φ_{H_2} of photolysis determined by the gas evolution rate ($\nu_{H_2} = 10^{13}$ molecules $H_2/cm^2 \cdot$ sec) and by the irradiation intensity ($I = 5 \cdot 10^{14}$ quanta/ $cm^2 \cdot$ sec) is about $4 \cdot 10^{-2}$. Deep photolysis (removal of hydrogen in 100–200 monolayers of LiH) decreases the quantum yield by one order of magnitude (Fig. 3b). No photosensitization of LiH occurs in the visible spectral region despite the appearance of absorption bands of F and V centers (6). The intensity dependence of the stationary photolysis rate during irradiation by monochromatic light ($\lambda = 254$ nm) is described by the relation $\nu_{H_2} = kI$, when the intensity varies from 10^{13} to $2 \cdot 10^{14}$ quanta/cm². Hydrogen evolution during LiH photolysis is thermally activated. The activation energy determined from the temperature dependence of the gas evolution rate equals 7.5 ± 0.5 kcal/mole in the temperature region 77–400 K.

As shown in Ref. (16), p-type photoconductivity in LiH is excited when it is irradiated by light with $\lambda < 300$ nm. We observed the kinetics of the photocurrent to be monotonic, with a characteristic time of response $\tau_{0.5} = 10$ sec (Fig. 1d). A stationary photocurrent value in unilluminated sam-
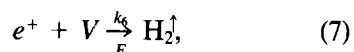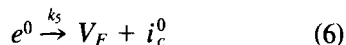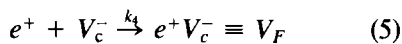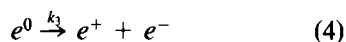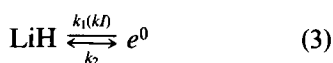
ples is attained more slowly than in those irradiated earlier (Fig. 1e). Annealing returns a sample to an initial state, probably due to the thermal release of holes and recovery of initial concentration of traps (cation vacancies can serve as traps).

Irradiation with uv light ($\lambda = 254$ nm) decreases the dark photoconductivity of LiH which is provided by cation vacancies (2, 10). Recovery of an initial conductivity value occurs slowly and takes approximately one day at room temperature. Variations of the dark conductivity during LiH photolysis have been measured by consequent illuminations (Fig. 4). Such a technique is correct as the characteristic times of photoconductivity and variations of the dark conductivity differ strongly. The rapid decrease of the concentration of cation vacancies during one minute ends by reaching a stationary value. The time during which the dark conductivity reaches its stationary value coincides with the time needed for the gas evolution rate to reach its maximum.

Discussion

All data presented indicate that during PCD in LiH, the processes of hydrogen evolution and charge transfer by cation vacancies are closely connected. We consider a possible kinetic scheme of LiH photolysis taking into account this circumstance as

well as the peculiarities of the electron excitations. It is known that during absorption of light quanta with 5 eV energy, excitons e^0 are generated in LiH (4). They can deactivate, decompose into free electron e^- and hole e^+, or produce structure defects due to electron–phonon interaction via an autolocalized state $Li_2^+e^+$ (7). In contrast with alkali–halide crystals, one does not observe in LiH the decomposition of electron excitations with formation of interstitial atoms or hydrogen ions and V_k centers—quasimolecules of the A_2^- type (17, 18). One of the possible ways of decomposition of an autolocalized exciton is the formation of unrelaxed V centers and Li_2^+ type quasimolecules. Although this mechanism has not been directly proved, it corresponds to a special type of autolocalization in case of LiH. Another possibility, formation of V_F centers, which has been detected by spectroscopic methods (19), is the capture of holes at cation vacancies. It is this process which accounts for the character of the variation of the dark conductivity during LiH photolysis and the effect of annealing of traps for photoholes observed in photoconductivity. It has been shown that the cross section for charged center capture by a neutral one is considerably larger than that by a center of the same charge sign (20). Therefore, of two ways of hydrogen formation—bimolecular hole recombination and recombination of holes with centers of the p type—the latter must be chosen. Taking into account the high absorption coefficient of LiH, it is natural to believe that photolysis proceeds in a kinetic rather than diffuse regime, i.e., hydrogen evolution is provided by the recombination of holes and V_F centers in a nearsurface layer. Thus, the whole set of electron–ion processes proceeding in LiH photolysis has the following form:

$$LiH \underset{k_2}{\overset{k_1(kI)}{\rightleftarrows}} e^0 \tag{3}$$

$$e^0 \overset{k_3}{\rightarrow} e^+ + e^- \tag{4}$$

$$e^+ + V_c^- \overset{k_4}{\rightarrow} e^+V_c^- \equiv V_F \tag{5}$$

$$e^0 \overset{k_5}{\rightarrow} V_F + i_c^0 \tag{6}$$

$$e^+ + V \underset{F}{\overset{k_6}{\rightarrow}} H_2^\uparrow, \tag{7}$$

where i_c^0 is an interstitial lithium atom bound in a Li_2^+ quasimolecule.

Taking into account the smallness of the quantum yield of LiH photolysis and rapid establishment of a quasistationary hole concentration, one obtains the following expression for the photolysis rate after solution of the system of differential equations:

$$\nu_{H_2} = \frac{dH_2}{dt} = k_6e^+V_F$$
$$= (A - B)\exp(-k_4e^+t) \tag{8}$$
$$- A\exp(-k_6e^+t) + B,$$

where

$$A = \frac{k_4k_6e^+V_c^0}{k_4 - k_6}, \qquad B = k_5e^0,$$

V_c^0 is the initial equilibrium concentration of cation vacancies. Analysis of this expression shows that at $t \rightarrow \infty$ a quasistationary photolysis rate

$$\nu_{H_2}|_{t\rightarrow\infty} = k_5e^0 = \frac{k_5}{k_2}\kappa I \tag{9}$$

is achieved, corresponding to the experimentally observed dependence on the irradiation intensity. The function $\nu_{H_2}(t)$ has a maximum at

$$t_m = \frac{1}{e^+(k_4 - k_6)}\ln\left[\frac{k_4}{k_6} \cdot \frac{A}{A - B}\right] \tag{10}$$

when $k_4 > k_6$ (the formation rate of recombination centers V does not exceed the rate of hydrogen formation) and for $k_4 \cdot k_6e^+V_c^0 > k_5e^0(k_4 - k_6)$. The variable V_c^0 enters the last inequality, and its variation can lead to the inequality reversal and disappearance

of the maximum. In fact, studies of the dark conductivity showed that decrease of the concentration of cation vacancies results in disappearance of the maximum on the kinetic curve of gas evolution rate. Annealing of a sample allows recovery of the initial equilibrium concentration of cation vacancies, and the rate of hydrogen evolution reaches its maximum again. In view of Fig. 4 we suppose the reduction of the equilibrium concentration of cationic vacancies to be the slow stage at room temperature. An increase in intensity moves the system from quasiequilibrium, and a new quasistationary rate of H_2 evolution is achieved through the maximum. The observed specificity of gas evolution kinetics during LiH photolysis is explained, therefore, by the existence of two ways of formation of recombination centers: capture of holes at a restricted number of available cation vacancies, and constant photogeneration of unrelaxed active V_F centers. Whereas the first channel contributes to photolysis at initial stages only, formation of structure defects during a photochemical reaction determines the stationary photolysis rate. The expression for $\nu_{H_2}(t)$ obtained above does not describe the gas evolution rate during the first 10–15 sec until a stationary flux of holes is established.

The activation energy value for the stationary gas evolution rate equals 7.5 ± 0.5 kcal/mole, and according to Eq. (9) is the activation energy for the decomposition of an autolocalized exciton $Li_2^+ e^+$ into structural defects.

On the basis of the suggested kinetic scheme for lithium hydride photolysis, several possible ways of regulating the LiH photolysis rate with the help of ionic defects can be considered. A traditional method of solid state chemistry—doping with doubly charged cations—can apparently be used for regulation of the initial gas evolution connected with a concentration of cation vacancies. As to the stationary photolysis rate, it must depend not only on the ionic defects available in a crystal, but on the existence of a concentration of other types of exciton traps as well. Particles of a solid product of photolysis can serve as such traps, their presence changing the efficiency of the radiative defect formation.

Acknowledgments

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