TRAPPING OF HYDROGEN ATOMS IN X-IRRADIATED SALTS AT ROOM TEMPERATURE AND THE DECAY KINETICS

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SUMMARY

Ten salts (hypophosphites, formates, a phosphite, a phosphate, and an oxalate) were X-irradiated, whereby hydrogen formed chemically by a radiolytic process becomes trapped in the solid. By room-temperature vacuum extraction, the kinetics for the evolution of this trapped hydrogen was studied mass spectrometrically. All salts except two exhibited second-order kinetics. The two exceptions (NaH$_2$PO$_2$·H$_2$O and K$_2$HPO$_4$) showed first-order kinetics. Based on experimental results, we postulated that the escape of hydrogen involves three steps: the diffusion of hydrogen atoms from the bulk to the surface, association of these atoms on the surface (rate controlling step for second-order hydrogen evolution), and the desorption of molecular hydrogen from the surface. The hydrogen does not escape if the irradiated salt is stored in air, apparently because adsorbed air molecules occupy surface sites required in the escape mechanism.

The effect of two parameters (sample size and presence of unirradiated salt) on the decay kinetics of irradiated nickel hypophosphite was also studied.

INTRODUCTION

During the γ-irradiation of hypophosphites (refs. 1 and 2), phosphites (ref. 3), and formates (refs. 4 and 5) atomic hydrogen (H·) appears to be produced:

\[
\begin{align*}
\text{H}_2\text{PO}_2^- & \xrightarrow{\text{hv}} \text{HPO}_2^- + \text{H}^+ \quad (1) \\
\text{HPO}_3^- & \xrightarrow{\text{hv}} \text{PO}_3^- + \text{H}^+ \quad (2)
\end{align*}
\]
These studies identified the ion radical produced, by means of electron paramagnetic resonance (EPR). It was assumed (ref. 4) that the hydrogen formed is lost rapidly from the irradiated salts as molecular hydrogen. Recent studies at Lewis Research Center (ref. 6) have shown that such reactions (eqs. (1) to (3)) probably take place during X-irradiation of the appropriate salts and that the hydrogen which is formed is trapped in the solid for considerable time periods (over 15 days).

The purpose of this present investigation was to study the nature of the trapping of the hydrogen in these salts. The study involved the measurement of the kinetics of hydrogen evolution from various X-irradiated salts. This measurement was accomplished by room-temperature vacuum extraction, with the rate of hydrogen evolution being determined mass spectrometrically. This investigation also included a study of the rate constant of hydrogen evolution for nickel hypophosphite as a function of sample weight.

**APPARATUS AND PROCEDURE**

Ten X-irradiated salts were studied: nickel hypophosphite \((\text{Ni(H}_2\text{PO}_2)_2\cdot6\text{H}_2\text{O})\), sodium hypophosphite \((\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O})\), ammonium hypophosphite \((\text{NH}_4\text{H}_2\text{PO}_2)\), cobalt hypophosphite \((\text{Co(H}_2\text{PO}_2)_2)\), calcium hypophosphite \((\text{Ca(H}_2\text{PO}_2)_2)\), anhydrous disodium hydrogen phosphite \((\text{Na}_2\text{HPO}_3)\), nickel formate \((\text{Ni(CHO}_2)_2\cdot2\text{H}_2\text{O})\), sodium formate \((\text{NaCHO}_2)\), nickel oxalate \((\text{NiC}_2\text{O}_4\cdot2\text{H}_2\text{O})\), and dipotassium hydrogen phosphate \((\text{K}_2\text{HPO}_4)\). The salts had in general about a 40-micrometer particle size.

The general format of the experimental investigation was as follows: A known quantity of the compound (less than a gram) was placed in an aluminum boat (inside dimensions, 5 cm by 0.6 cm by 0.6 cm; wall thickness, 0.1 cm). The use of a platinum or gold boat in place of an aluminum boat did not alter the results. The sample was exposed for about 1 hour to 250-kilovolt, 10-milliampere X-rays from a tungsten target tube with the sample 10 centimeters from the target. This dose rate was found to be 660,000 roentgens per hour. The actual exposure time (which determined the dose) and the actual weight of the sample were selected to produce easily measurable rates for the hydrogen gas evolution.

Within 5 minutes after irradiation the measurement of the gas evolved at room temperature (about \(23^\circ\pm1^\circ\ C\)) by vacuum extraction was begun. For this purpose a modification of the method used in an earlier work (ref. 6) proved to be satisfactory. The aluminum boat containing the irradiated sample was placed in a 10-centimeter-long glass tube with a 19/38 standard taper joint at the top. This tube was connected to the mani-
fold of the apparatus as depicted in figure 1 and evacuated by the auxiliary pump for 15 seconds. Immediately after this, the evolved gas was pumped into the expansion volume of the mass spectrometer by means of a three-stage mercury diffusion pump. A liquid nitrogen trap between the pump and the sample prevented condensible vapors such as water from entering the expansion volume. After the gas had been collected for a known period of time (length of first collection, several minutes), the amount of hydrogen present in the collection volume was determined quantitatively with the mass spectrometer. The collection sample was then discarded (pumped out). The second collection of hydrogen was begun immediately, and after another known (longer) period of time the amount of hydrogen was determined. This procedure was repeated until the rate of hydrogen collection approached the low value for the collection system alone (blank value). Generally, the procedure involved about 20 collections during the day followed by a final overnight collection. The collected gas was composed of essentially pure hydrogen.

A Consolidated Electrodynamics Corporation Model 21-614 mass spectrometer was used. The calibrated system, discussed previously (ref. 7), was sensitive to nanogram quantities of hydrogen. The amount of hydrogen collected during each time period was corrected for both the mass spectrometer background (about 4 ng of hydrogen per determination) and the collection system blank (about 24 ng/hr).

The effect of two parameters on the kinetics of hydrogen evolution was studied using X-irradiated Ni(H₂PO₂)₂·6H₂O. These parameters were sample size (0.0039 to 0.67 g) and presence of some unirradiated Ni(H₂PO₂)₂·6H₂O (0.014 g irradiated mixed with 0.2 g unirradiated).

RESULTS

Figure 2 shows typical hydrogen evolution data for small samples of X-irradiated Ni(H₂PO₂)₂·6H₂O. These data indicate second-order kinetics:

\[ \sqrt{\frac{dc}{dt}} = \sqrt{k \cdot C} \]

or

\[ \frac{dc}{dt} = -kC^2 \]
where \( k \) is the rate constant. The square root of the hydrogen evolution rate \( \sqrt{-dC/dt} \) is plotted against \( C_0 - C \) and \( C \), where \( C \) is the hydrogen concentration remaining in the sample and \( C_0 \) is its initial concentration. Initially the curve deviates from linearity. This initial deviation is more pronounced for larger samples and for the mixture of irradiated and unirradiated material. Other than this, data for all the samples of irradiated \( \text{Ni(H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O} \) tested had the same general appearance shown in figure 2, that is, second-order kinetics for the evolution of hydrogen.

From a graph of \( \sqrt{-dC/dt} \) against \( C_0 - C \), such as figure 2, the initial concentration \( C_0 \) is readily obtained from the X-intercept. The rate constant \( k \) is likewise readily obtained from such a plot (fig. 2) by squaring the slope. See equation (4). In figure 3 the values of \( k \) for \( \text{Ni(H}_2\text{PO}_2)_2 \cdot 6\text{H}_2\text{O} \) are plotted as a function of the sample weight. Except at low sample weights, \( k \) is essentially constant \((3.7 \times 10^4 \text{ g samp} \cdot \text{g H}_2 \text{O} \text{ hr}^{-1})^{-1}\) with good reproducibility. However, for low sample weights, \( k \) appears to be larger and less reproducible.

The kinetics found for the evolution of hydrogen from each salt investigated are given in table I. With two exceptions (i.e., \( \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} \) and \( \text{K}_2\text{HPO}_4 \)), the kinetic behavior was second order. Irradiated \( \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} \) and \( \text{K}_2\text{HPO}_4 \) showed first-order behavior for hydrogen evolution

\[
\frac{-dC}{dt} = k C \tag{5}
\]

This behavior is depicted graphically in figure 4 for \( \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} \). The rate constants for both the first- and second-order kinetic processes are listed in table I. The second-order constants ranged from \( 10^4 \) to \( 10^7 \) grams of sample per gram of hydrogen per hour.

DISCUSSION

The fact that the hydrogen evolution kinetics for most of the irradiated salts is second order led us to postulate the following escape mechanism:

\[
H^\cdot (\text{trapped in bulk}) \rightarrow H^\cdot (\text{surface}) \tag{6}
\]

\[
2H^\cdot (\text{surface}) \rightarrow \text{H}_2 (\text{surface}) \tag{7}
\]

\[
\text{H}_2 (\text{surface}) \rightarrow \text{H}_2 (\text{gas}) \tag{8}
\]
with equation (7) generally being the rate controlling step. But irrespective of the exact mechanism, second-order kinetics strongly suggests that atomic hydrogen is involved in the escape mechanism.

Because the amount of hydrogen liberated from a sample is too large to be accountable to purely surface adsorption, we are led to postulate that most of the hydrogen is held within the bulk of the crystal. By using a value of $54 \times 10^{-12}$ gram of H· per gram of Ni(H$_2$PO$_2$)$_2$·6H$_2$O (ref. 6), a typical dose of $10^6$ roentgens, and an actual crystal size of 40 micrometers, it can be shown that 150 atoms of hydrogen would have to be adsorbed on each surface molecule. This ratio of adsorbed H· per molecule of substrate is far too high for a solely surface adsorption phenomena.

Because the association of hydrogen atoms on the surface (eq. (7)) is rate controlling, the mobility of hydrogen atoms from inside the crystal to the surface must be high enough to prevent this process (eq. (6)) from significantly affecting the overall kinetics. Likewise the removal of hydrogen from the surface must also be relatively fast.

For the two salts, which exhibit first-order kinetics for hydrogen evolution, NaH$_2$PO$_2$·H$_2$O and K$_2$HPO$_4$, the mechanism proposed in reactions (6) to (8) can also be applied. However, for these salts, reaction (8) (a first-order reaction) is most likely the rate controlling step.

This trapping of hydrogen atoms in irradiated nonmetallic solids is not unique. Other investigators have identified, by EPR, trapped hydrogen in $\gamma$-irradiated frozen solutions (about 70K) of sulfuric acid (ref. 8), perchloric acid (ref. 9), and phosphoric acid. Trapped hydrogen atoms have also been detected by EPR at room temperature in $\gamma$-irradiated phosphates (ref. 10). Our present study, however, is the most definitive one on the decay kinetics of the trapped hydrogen atoms.

We have reported previously (ref. 6) that hydrogen formed during the irradiation of salts (e.g., Ni(H$_2$PO$_2$)$_2$·6H$_2$O) remains trapped in the solid for a considerable time. Practically no trapped hydrogen is lost when X-irradiated Ni(H$_2$PO$_2$)$_2$·6H$_2$O stands for 15 days in air. Nevertheless, trapped hydrogen is rapidly evolved when irradiated salts are subjected to vacuum conditions. Apparently the adsorption of air molecules (e.g., N$_2$, O$_2$, CO$_2$, and/or H$_2$O) on the solid inhibits hydrogen atoms present in the interior of a crystal from occupying the surface sites necessary for hydrogen escape.

As mentioned previously, the hydrogen atoms are quite mobile within the bulk. Their mobility on the surface should be even greater because of shallower potential wells, assuming of course vacuum conditions so that surface sites are not blocked by air molecules. Under such conditions, migration of hydrogen atoms from one crystal to another is possible if the crystals are in contact. By such a process, a sample originally nonuniform in hydrogen concentration (e.g., large samples of ref. 6 or intentionally prepared nonuniform mixtures) could become more uniform. When near uniformity is achieved, second-order kinetics for hydrogen evolution should be observed.
However, prior to this condition, diffusion along the surface may be so rapid that the hydrogen activity on the surface is not in equilibrium with the hydrogen concentration in the bulk. Under such circumstances, deviation from second-order kinetics should be expected. Our results show that indeed large initial deviations from second-order kinetics are found for large (nonuniform) samples and for mixtures purposely made non-uniform in hydrogen atom concentration.

The rate constant $k$ for second-order hydrogen evolution from $\text{Ni(H}_2\text{PO}_2\text{)}_2\cdot6\text{H}_2\text{O}$ (fig. 3) appears to increase abruptly from a constant value ($k = 3.7 \times 10^4 \text{ s}^{-1}\text{g}^{-1}\text{H}_2\text{O}^{-1}\text{hr}^{-1}$) as the sample weight decreases below about 0.05 gram. We attribute the high values of $k$ to experimental circumstances and not to an actual increase in the rate constant. We believe that some of the hydrogen may be desorbed via aluminum boat and glass surfaces. For large samples the percent contribution would likely be small. However, for small samples, such an effect may contribute noticeably to the overall evolution of hydrogen. The net effect would be a high apparent value of $k$ for small sample weights.

**RESUMÉ OF PROCESS INVOLVED**

When certain salts (e.g., hypophosphites) are X-irradiated, hydrogen atoms are produced. At atmospheric pressure, adsorbed air molecules prevent their association and so atoms of hydrogen are trapped within the crystalline lattice. Under vacuum conditions, the hydrogen atoms diffuse to the surface (being very mobile), and recombine at surface sites; the resultant hydrogen molecules escape as a gas. For most salts investigated the recombination is the slowest step; this results in second-order kinetics.

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**REFERENCES**


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### TABLE I. - KINETIC DATA FOR HYDROGEN EVOLUTION FROM X-IRRADIATED SALTS

<table>
<thead>
<tr>
<th>Salt</th>
<th>Reaction order</th>
<th>Rate constant, k</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni(H}_2\text{PO}_2\text{)}_2 \cdot 6\text{H}_2\text{O} )</td>
<td>Second</td>
<td>3.7x10⁴</td>
</tr>
<tr>
<td>( \text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O} )</td>
<td>First</td>
<td>------</td>
</tr>
<tr>
<td>( \text{NH}_4\text{H}_2\text{PO}_2 )</td>
<td>Second</td>
<td>10⁷</td>
</tr>
<tr>
<td>( \text{Co(h}_2\text{PO}_2\text{)}_2 )</td>
<td>Second</td>
<td>6x10⁴</td>
</tr>
<tr>
<td>( \text{Ca(h}_2\text{PO}_2\text{)}_2 )</td>
<td></td>
<td>6x10⁴</td>
</tr>
<tr>
<td>Anhydrous  ( \text{Na}_2\text{HPO}_3 )</td>
<td></td>
<td>10⁶</td>
</tr>
<tr>
<td>( \text{Ni(CHO}_2\text{)}_2 \cdot 2\text{H}_2\text{O} )</td>
<td></td>
<td>10⁵</td>
</tr>
<tr>
<td>( \text{NaCHO}_2 )</td>
<td></td>
<td>10⁶</td>
</tr>
<tr>
<td>( \text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} )</td>
<td></td>
<td>10⁷</td>
</tr>
<tr>
<td>( \text{K}_2\text{HPO}_4 )</td>
<td>First</td>
<td>------</td>
</tr>
</tbody>
</table>

\( g_{\text{samp}}(g_{\text{H}_2})^{-1}(\text{hr})^{-1} \) \( \text{hr}^{-1} \)
Figure 1. - Schematic drawing of desorption chamber and pumping system.
Figure 2. - Rate of hydrogen evolution from X-irradiated Ni(H_2PO_4)_2·6H_2O. Sample size, 0.0105 gram; voltage, 250 kilovolts; current, 10 milliamperes; dose, 1.3x10^6 roentgens.

Figure 3. - Effect of weight of X-irradiated Ni(H_2PO_4)_2·6H_2O on rate constant for hydrogen evolution.
Figure 4. - Rate of hydrogen evolution from X-irradiated NaH$_2$PO$_4$·H$_2$O. Sample size, 0.0195 gram; voltage, 250 kilovolts; current, 10 milliamperes; dose, 6.6x10$^5$ roentgens.