fonate in their respective ammonolytic products, the following series is obtained

$C_5H_5N \cdot SO_3 > C_6H_5N(CH_3)_2 \cdot SO_3 > O(CH_2CH_2)_2O \cdot SO_3$
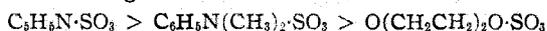
This is also the order of their decreasing stability toward water.[1,4] In view of the fact that imido-disulfonate only is formed when ammonia and sulfur trioxide react, it is logical to conclude that the presence of this product is due to the ammonation of sulfur trioxide held but loosely by the donor molecule. Consequently, the less stable the sulfur trioxide complex, that is, the weaker the co-ordinate bond holding the sulfur trioxide molecule, the greater will be the proportion of imidodi-sulfonate in the ammonolytic product.

Summary

Reactions of liquid ammonia with sulfur tri-oxide addition compounds result primarily in the formation of ammonium sulfamate. These reactions are considered to be ammonolytic in character.

The Photochemical Decomposition of Solid Hydrogen Compounds at Low Temperatures

BY L. FARKAS, Y. HIRSHBERG AND L. SANDLER

Very little has been known previously of the photochemical decomposition of solids at low temperatures.[1,2] It seemed, therefore, worth while to investigate reactions involving the liberation of hydrogen, since the ortho–para concentration of the hydrogen may reveal interesting features of the decomposition mechanism. It is well known that below 200°K. the ortho–para ratio of equilibrium hydrogen is dependent on the temperature and thus this ratio may indicate at which effective temperature the photochemical formation of the hydrogen has taken place.

In the following some experiments on the photochemical decomposition of hydrogen iodide, formaldehyde and methyl alcohol at temperatures between 65° and 85°K. are reported. All these substances give off hydrogen (besides other reaction products) when decomposed photochemically.[1,3,4]

Experimental

Hydrogen iodide was prepared in the usual way by catalytic combination of hydrogen with iodine and repeated fractional distillation at low temperatures.[5] It was kept in a glass bulb and was perfectly white in the solid state. Apiezon grease was used for the taps, which was only slowly attacked by hydrogen iodide.

The methyl alcohol was the purest obtainable product. As a source of formaldehyde. the vapor of 40% aqueous solution was used.

The experimental arrangement is shown in Fig. 1. The hydrogen iodide, formaldehyde or methyl alcohol was condensed on spot S of tube V, which contained liquid air. The glass tube was specially thin at S, in order to improve the heat exchange between the condensed substance and the liquid air. The amount of substance on S was adjusted by a lock system between the tap T and the storage bulb so as to form a white circle of about 5 mm. diameter and of about 10,000–100,000 molecular layers. A mercury arc served as a light source and the ultraviolet light entered through the quartz window Q opposite the spot S.
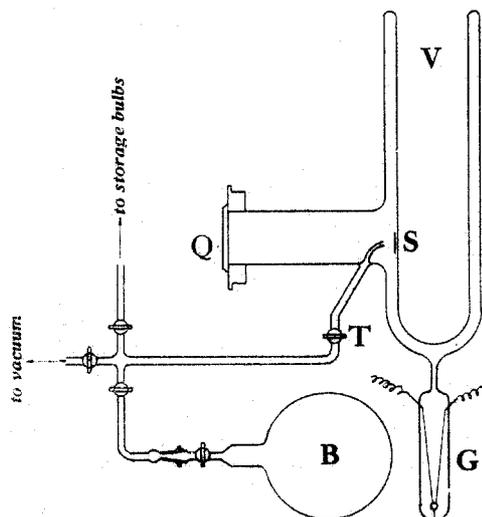
Fig. 1.

Occasionally the temperature of the tube was lowered to 65° K. by pumping off the liquid air. After the substance was condensed into the reaction vessel, the tap T was closed and the evolution of hydrogen during the illumination followed up by the Pirani gage (G). The illumination was continued until 30–40 cu. mm. of gas at S. T. P. was

(1) Bonhoeffer and L. Farkas, Z. physik. Chem., 132, 235 (1928).
(2) Hilsch and Pohl, Ann. Physik, [5] 32, 155 (1938).
(3) Cf. Loecker and Patat, Z. physik. Chem., B27, 431 (1934).
(4) Patat, Z. Elektrochem., 41, 494 (1935).
(5) Cf. Farkas and Melville, "Experimental Methods in Gas Reactions," The Macmillan Co., New York, 1939, p. 160.

evolved. The lamp was then switched off and the gas collected in a large bulb (B). The analysis of the ortho-para composition of the hydrogen was carried out by the micro-conductivity method.[6]

Experiments with Hydrogen Iodide.—During the illumination only a small amount of gas was given off by the hydrogen iodide crystals; the greater part of the photo-chemically formed hydrogen remained trapped in the solid. All the gas was given off immediately when the liquid air level in the tube V was lowered below the spot (S), as then the substance sublimed to the lower part of the tube.

TABLE I

No.	Time of illumination. min.	Temp., °K.	% p-H_2	Equilibration %
1	70	85	34.3	46
2	30	~70	38.6	~44
3	35	65	40.8	45
4	36	85	34.5	47
5	30	85	33.8	44
6	195	85	37.6	63
7	45	85	35.8	54

Experiments 1 and 4 (Table I) show that at 85°K. the evolved hydrogen contained 34% para-hydrogen corresponding to an ortho–para ratio in equilibrium at 115°K.[7]

In order to test the possibility of a secondary ortho–para conversion taking place after the illumination, normal hydrogen was introduced into the reaction vessel. It was found, however, that no conversion to para-hydrogen occurred in the presence of the hydrogen iodide crystals. When the hydrogen trapped inside the crystals was left in them for one hundred and fifty minutes at 85°K. after the illumination had been switched off (expt. 5), no change in the para-hydrogen concentration was observed, showing the absence of any secondary para–ortho conversion within the solid in the "dark." All these experiments show definitely that the formation of the para-hydrogen takes place during the illumination and the para–ortho concentration is in some way determined by the tempera-ture of the solid hydrogen iodide.

By lowering the temperature of the liquid air to 70–65°K. (expt. 2 and expt. 3), para-hydrogen of higher concentration than in expts. 1 and 4 was obtained, the percentage of "equilibration," however, was the same as before. These experiments prove that the para-hydrogen is formed inside the solid during the illumination and not at the time when it is given off by the solid. The temperature at which the sublimation took place was the same in all experiments.

The simplest explanation for the fact that the apparent "equilibration" is not complete is that the actual tempera-ture of the solid during the illumination is higher than that of the liquid air in the tube V. Experiments 6 and 7 show indeed that there is a marked increase in the para-hydrogen concentration of the evolved hydrogen if the amount of heat transferred from the outside or from the source to the illuminated substance is diminished. This was obtained (1) by reducing the light intensity of the mercury lamp through intensive cooling and through increasing the

distance between reaction vessel and light source (in expt. 6), (2) by cutting off the infrared radiation by a water filter, (3) by shielding the reaction vessel with tin foil against temperature radiation from outside and (4) by removing continually the gas evolved during the illumina-tion (in expt. 7). These experiments indicate that the para-hydrogen content of the gas formed during the de-composition corresponds nearly or completely to the tem-perature of the solid hydrogen iodide.

Experiments with Formaldehyde and Methyl Alcohol.—In the photochemical decomposition of formaldehyde hydrogen and carbon monoxide are formed.[3] There is also a possibility of carbon monoxide formation in the photoly-sis of methyl alcohol by secondary decomposition of the formaldehyde primarily formed.[4] The carbon monoxide was removed from the evolved gas by a cuprous chloride-ammonia solution.[8]

It was found that in all cases normal hydrogen was evolved (see Table II).

TABLE II

No.	Substance	Time of illumination. min.	Temp., °K.	% p-H_2
1	H_2CO	150	85	25
2	CH_3OH	110	85	25
3	CH_3OH	300	85	25
4	CH_3OH	300	75	25

Discussion of the Experiments with Hydrogen Iodide.—The photochemical decomposition of gaseous hydrogen iodide takes place according to the mechanism[1,9]

$$HI + h\nu \longrightarrow H + I \qquad (1)$$
$$H + HI \longrightarrow H_2 + I \qquad (2)$$
$$I + I \longrightarrow I_2 \qquad (3)$$
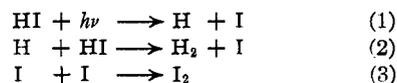
The same decomposition takes place also in the liquid[10] and the solid state.[1]

The present experiments have shown that the para–ortho ratio of the hydrogen formed corre-sponds to the temperature of the solid.

There are two different processes which may bring about the equilibration of the photochemi-cally formed hydrogen. One is the catalytic con-version of hydrogen under the influence of the inhomogeneous magnetic field of the iodine atom[11] and the other the reaction (2).

The iodine atom has a paramagnetic ground level $^2P_{i/_2}$ and it was shown by Rosenbaum and Hogness[12] that the conversion of para-hydrogen in the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is caused by the

(6) A. Farkas. *Z. physik. Chem.*. **B22**, 344 (1933).

(7) *Cf.* A. Farkas. "Orthohydrogen. Parahydrogen and Heavy Hydrogen." Cambridge University Press. 1935. p. 14.

(8) The standard solution of cuprous chloride–ammonia. as used in gas analysis. removes carbon monoxide quantitatively from an H_2 + CO mixture also at low pressures (~ 10^{-2} mm.) without converting para-hydrogen at an appreciable rate (see forthcoming publication).

(9) Warburg, *Ber. Berl. Akad.*, 314 (1916); 300 (1918).

(10) Bodenstein and Lieneweg. *Z. physik. Chem.*. **119**, 123 (1926).

(11) L. Farkas and Sachsse. *Z. physik. Chem.*. **B23**, 1 (1933).

(12) Rosenbaum and Hogness. *J. Chem. Phys.*. **2**, 267 (1934).

paramagnetic action of the iodine atoms present in thermodynamic equilibrium concentration.

A very rough calculation shows that an equilibration by the reaction

$$I + o\text{-}H_2 \rightleftarrows I + p\text{-}H_2 \qquad (4)$$
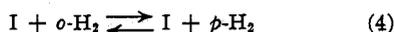
is only possible if the relevant conditions for the conversion in the solid are very favorable. The lower limit for the theoretical half-life time is given by

$$\tau_{\text{theor.}} = 0.69/W_{\text{solid}}Z_{\text{solid}}[I] \qquad (5)$$

(W_{solid} the transition probability $p \rightleftarrows o$ per collision, Z_{solid} the collision frequency between H_2 and I in the solid, [I] the stationary concentration of the iodine atoms), if for W_s, Z_s, [I] the upper limits are used.[13]

W_{solid} is, as a first approximation, equal to $W_{\text{gas}} = 4 \times 10^{-12}$. For the calculation of Z_{solid}, the approximation of Rabinowitch[14] is used according to which $Z_{\text{solid}} = Z_{\text{coörd.}} \cdot \nu$, $Z_{\text{coörd.}}$ denoting the number of coördinations of the pair $H_2 + I$ per second and ν the number of vibrations during a coördination. In this formula it is assumed that each vibration during the coördination is equivalent to a collision in the gas. The order of magnitude of Z is 3×10^{12} sec.$^{-1}$mole^{-1}.[15]

The upper limit for [I] will be obtained by considering their production and recombination by diffusion. The time necessary for a particular iodine atom to diffuse the mean distance $\bar{x} = 1/[I]^{1/3}$ between two iodine atoms is given by the expression $t = \bar{x}^2/2D = 1/2D[I]^{2/3}$. Then the iodine atom under consideration will be somewhere on the surface of a sphere with a radius $\bar{x}$. It will collide with another iodine atom with the probability $\sim 4a_I^2/\bar{x}^2$ (coördination number $= 8$, $\pi a_I^2 = 10^{-15}$ cm.^{2} is the cross section of the iodine atom).

If n iodine atoms are formed per sec., and cm.^{3}, and [I] $= nt_0$, t_0 being the mean life time of an iodine atom, t_0 will be given by the expression

$$(nt_0)^{-1/3} = 8Dt_0 a_I^2 (nt_0)^{2/3}$$

Using the values $D = 10^{-11}$ cm.^{2} sec.$^{-1}$ and $n = 3 \times 10^{17}$ sec.$^{-1}$ cm.$^{-3}$ (calcd. from the rate of decomposition) one obtains $t_0 = 6$ min. and [I] $= 1.8 \times 10^{18}$ cm.$^{-3}$ $= 3 \times 10^{-3}$ mole/l. On the

(13) In the following it is assumed that the hydrogen is dissolved in the solid in molecular form. If microscopic bubbles are formed inside the crystals, the rate of conversion would appear diminished.

(14) Rabinowitch. *Trans. Faraday Soc.*, **33**, 1225 (1937).

(15) According to L. Farkas and U. Garbatski [*Trans. Faraday Soc.*, **35**, 263 (1939)], the rate of conversion of para-hydrogen in presence of nitric oxide in aqueous solution is much slower than the rate corresponding to $Z_{\text{liquid}} = Z_{\text{coörd.}} \times \nu$.

basis of these figures the half-life time in the solid is $\tau_{\text{theor.}} = 20$ min.

Since expts. 1, 3 and 4 have shown that the equilibration of hydrogen is (nearly) completed during the illumination, it is obvious that the half-life time of the conversion must be small compared with the time of illumination. Putting $\tau_{\text{exptl.}}$ at least one-sixth of the time of illumination, i. e., 300 min., $\tau_{\text{theor.}}$ seems compatible with the experimental result. The margin between these figures, however, is not very large and owing to the nature of simplifications made in the calculation of $\tau_{\text{theor.}}$, the value obtained seems far too small. The authors believe that the conversion by the action of iodine atoms is not likely to be the decisive process for the equilibration.

The other possibility for the equilibration is reaction (2). In this reaction about 30,000 cal. are evolved. This circumstance makes it difficult to understand that in this process equilibrium hydrogen of low temperature should be formed, as the heat evolved in the reaction should raise the effective temperature of the particles concerned. Hydrogen corresponding to a low temperature equilibrium could only be formed if the heat of reaction is completely dissipated during the collision H + HI$_{\text{solid}}$ and is taken up by the whole hydrogen iodide lattice. Although at present we have no information of the energy exchange in this type of reaction, the present experiments seem to indicate that such dissipation of energy actually occurs.

Discussion of the Experiments with Formaldehyde and Methyl Alcohol.—The photochemical decomposition of formaldehyde takes place according to

$$HCHO + h\nu \longrightarrow CO + H_2 \qquad (6)[3]$$

Two different mechanisms have been suggested for the primary process involved in the photolysis of formaldehyde

$$H_2CO + h\nu \longrightarrow H_2 + CO \qquad (7)[3]$$
$$H_2CO + h\nu \longrightarrow 2H + CO \qquad (8)[16,17]$$
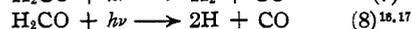
The photolysis of methyl alcohol takes place according to

$$CH_3OH + h\nu \longrightarrow CH_2O + H_2 \qquad (9)$$

and equations analogous to (7) and (8) can be considered as primary processes of this reaction.

If the hydrogen atoms formed in reaction (8) would react with another formaldehyde molecule according to

(16) Norrish, *Nature*, **141**, 1138 (1938).

(17) Bergmann and Samuel, *ibid.*, **141**, 832 (1938).

$$H + H_2CO \longrightarrow H_2 + H\dot{C}O \qquad (10)$$
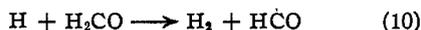
one might expect the formation of para-hydrogen as found in the decomposition of hydrogen iodide. Thus the absence of para-hydrogen formation can be regarded as excluding the step (10). Consequently the conclusion offers itself that, whichever the actual primary process may be, (7) or (8), the two atoms forming a hydrogen molecule must come from the same parent formaldehyde molecule. The state of affairs in the photolysis of methyl alcohol is exactly analogous.

As no detailed knowledge about the energy exchange during collisions in solids is yet available, one cannot decide between the primary reactions (7) and (8) on the basis of the present experiments. The suggestion that a dissipation of energy takes place at collisions within a solid, as proposed for the reaction $H + HI_{solid}$, would favor mechanism (7) according to which no such dissipation of energy can occur.

Summary

It is found that para-hydrogen is formed when irradiating solid hydrogen iodide at low temperatures. Two explanations are given and discussed: (a) the hydrogen primarily formed can be converted by the paramagnetic action of free iodine atoms; (b) the heat formed in the reaction $H + HI_{solid} = H_2 + I$ is dissipated in the solid. In the photolysis of formaldehyde and methyl alcohol under the same conditions normal hydrogen is formed. This seems to indicate that the two hydrogen atoms forming a molecule are coming from the same formaldehyde or methyl alcohol molecule.

The Catalytic Interaction of Acetylene and Hydrogen on Platinum

BY A. FARKAS AND L. FARKAS

In a series of communications the catalytic hydrogenation of ethylene,[1] benzene[2] and acetone[3] on platinum was investigated. In the first two examples, the hydrogenation consists of the addition of hydrogen to a double bond. In the case of acetone the reduction reaction can be


Fig. 1.—Hydrogenation of acetylene: expt. 16, 25 mm. $C_2H_2 + 60$ mm. H_2 at 101°; expt. 19, 21 mm. $C_2H_2 + 49$ mm. H_2 at 97°.

envisaged as a similar type of process. In the present communication the hydrogenation of acetylene was investigated under similar con-

ditions, this reaction being chosen as representative of hydrogen addition to triple bonds.

Experimental

The general experimental technique was similar to that previously described.[1] A platinized platinum foil (10 × 10 mm.) was used as the catalyst in a reaction vessel of 75 cc. volume. Hydrogen and acetylene were admitted to the reaction vessel through a U-tube kept at −80°. Acetylene was prepared from calcium carbide and purified according to the usual method.[4]

Dependence of the Hydrogenation on Pressure.—In some experiments, first acetylene was admitted to a given pressure and then condensed in a thin side-tube. Subsequently hydrogen was introduced and then acetylene quickly evaporated, the reaction time being calculated from this moment. The progress of the reaction under these conditions is shown in Fig. 1 (expt. 16). The reasons for the sudden drop in the pressure in the first half minute

(1) Farkas and Farkas, THIS JOURNAL, **60**, 22 (1938).
(2) Farkas and Farkas, Trans. Faraday Soc., **33**, 827 (1937).
(3) Farkas and Farkas, THIS JOURNAL, **61**, 1336 (1939).

(4) Farkas and Melville, "Experimental Methods in Gas Reactions," Macmillan and Co., Ltd., London, 1939, p. 167.