J. Chem. Soc. (A), 1971

The Reactions of Hydrogen Atoms with Solids at Low Temperature. Part I. Apparatus, Hydrocarbon, and Hydrogen Cyanide Reactions

By P. M. A. Sherwood and J. J. Turner,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

A novel apparatus is described for the production of a high density stream of hydrogen atoms and the investigation of the reactions of these atoms with solids at low temperature by i.r. spectroscopy. A critical analysis of the technique is made and its application to the study of the reactions of hydrogen atoms with hydrocarbons and hydrogen cyanide is described. A new reaction with *trans*-but-2-ene is described. Solid hydrogen cyanide reacts at low temperatures with hydrogen atoms to form an intermediate which may be CH₂=NH.

THE reactions of hydrogen atoms with compounds (e.g. HCN, SO₂, C₂N₂) at low temperature (ca. 77 \tilde{K}) were first investigated by Geib and Harteck; 1 their conclusions were limited by the techniques then available and also by the possibility of at least some gas-phase reaction. More recently reactions of hydrogen atoms with solid olefins and other hydrocarbons have been investigated by the techniques developed by Klein and Scheer,^{2,3} involving (1) kinetic studies of hydrogen uptake, (2) product analysis involving e.s.r. radical investigation at 77 K; and (3) gas phase analysis (g.l.c.) at room temperature. In most cases the hydrogen atoms have been generated by pyrolysis on a tungsten wire, or electric discharge (low frequency or microwave); some studies have, however, involved hydrogen-atom generation in the solid reactant at 77 K by photolysis of entrapped hydrogen iodide. Photolytically produced atoms are very energetic, but hydrogen iodide may react with the substrate (e.g. it reacted with the alkenes we studied).

Direct product identification at 77 K would improve the data available and allow the detection of any species stable at 77 K but unstable at higher temperatures. Herman and Giguere ⁴ used i.r. spectroscopy to study the reaction of hydrogen atoms (from a microwave discharge) with condensed ozone. We have developed a simple apparatus which allows a study of the i.r. spectra of solids at 77 K bombarded with energetic hydrogen atoms produced by a low frequency electric discharge to be made. Here we describe the apparatus together with experiments on solid olefins and observations on the reaction with solid hydrogen cyanide.

EXPERIMENTAL

Figure 1a is a schematic representation of the apparatus. The apparatus is evacuated (10^{-4} mmHg) through Q. The central caesium iodide window is firmly 'embedded ' in the solid copper block (Figure 1b). A compound, volatile at room temperature, but involatile at 77 K, can be condensed on the cold caesium iodide window via A (Figure 1b), with no discharge or hydrogen flow. Rotation of the central Dewar, about a ground-glass joint (not shown) allows the i.r. spectrum to be taken with the beam passing through X-Y. The window is repositioned perpendicular to the P-O direction (Figure 1a); hydrogen of high purity (99.999%) is passed in the direction P-Q and pumped out through Q, the pressure in the cell being maintained at 0.2 mmHg, and a discharge being struck between electrodes E_2 and E_3 of ca. 2000 V and 2 mA. This exposes the solid to highly energetic hydrogen atoms.

In the first experiments with condensed solids and hydrogen atoms from an E_2 to E_3 discharge, the resulting i.r. spectra were swamped by bands due to ice. This ice is formed by reaction of hydrogen atoms with the glass, since argon discharges produced virtually no ice and deuterium discharges (Matheson CP grade) gave intense bands due to D_2O_{ice} . We found that by water cooling the glass surrounding the electrodes and lead-in tubes virtually no ice was formed in subsequent experiments. A scale diagram

2474

¹ K. H. Geib and P. Harteck, Ber., 1933, 66, 1815.

² R. Kleim and M. D. Scheer, J. Amer. Chem. Soc., 1958, 80, 1007.

 ³ R. Klein and M. D. Scheer, J. Phys. Chem., 1958, 62, 1011.
⁴ K. Herman and P. A. Giguere, Canad. J. Chem., 1968, 46, 2649.

of the final apparatus, which has only two electrodes for the E_2 and E_3 discharges of the major experiments, is shown in Figure 2.

The electrical discharge was maintained for periods of 10 min (for a total of 50 min) separated by 5-min intervals to



FIGURE 1 Schematic representation of apparatus. (a) Elevation of cell. (b) Plan of cell showing spray-on tube, rotation of the central window, and the path of the infra-red beam. (c) Plan of cell showing the discharge path

permit cooling of the electrodes, glassware, and specimen; this also minimised ice formation.

Conduction of thermal energy by the hydrogen, and transfer of thermal energy from the plasma of the discharge together with the bombardment by discharge species will tend to raise the temperature of the exposed surface of deposited solid above the 77 K of the liquid nitrogen. A thermocouple embedded in the side of the central caesium iodide window with Wood's metal read ca. 113 K, although we believe the true temperature to be lower because of differences in thermal conductivity of the deposited solid and the thermocouple (Wood's metal). It is significant that solids with finite vapour pressures at 100 K stayed on the window. The 3-methylbut-1-ene, trans-but-2-ene, and propane used in this work was supplied by Matheson Gases. The hydrogen cyanide was prepared by reaction off 50%sulphuric acid with potassium cyanide.

Perkin-Elmer 521 and 457 spectrometers were used to record all infra-red spectra.

Preliminary Observations

Argon Discharges .--- For condensed solids no spectral changes of the type seen after hydrogen discharges (described below) have been observed on exposing them to argon discharges; this shows that spectral changes observed following hydrogen discharges cannot be due to electron bombardment.

⁵ J. C. Robb and H. W. Melville, Discuss. Faraday Soc., 1947,

132. ⁶ H. W. Melville and J. C. Robb, *Rev. Inst. franç. Pétrole*,

The Effect of the Distance of the Window from the Discharge.—The discharge between the electrodes E_2 and E_3 described above exposes the solid to highly energetic hydrogen atoms, probably in the ground electronic state since the discharge skirts round the window and block (Figure 1c) so that the solid on the window is not actually in the plasma. It should be noted that the source of generation of the atoms (the discharge) is very close to the solid, much closer than the source of generation of thermal hydrogen atoms in most experiments since a wire at 1000-2000 K would soon melt the solid if too close. The importance of having the source of generation close to the reactant can be illustrated by covering the window with a film of solid molybdenum trioxide: since MoO₃ is a solid this experiment can be performed with no liquid nitrogen cooling. On striking a discharge between E_2 and E_3 with hydrogen flowing, the MoO₃ turned deep blue in a matter of seconds [MoO₃ detects hydrogen atoms 5-8 by formation 9 of Mo₄O₁₀(OH)₂].

If the source is now placed further from the reactant, e.g. by striking the discharge between E_1 and E_2 (Figure 1a), there will be an appreciable loss of hydrogen atom energy and concentration. This is illustrated by repeating the MoO₃ experiment but this time with the discharge struck between E_1 and E_2 (Figure 1a); no change in colour in



 MoO_3 was observed after a considerable discharge time. No doubt this situation could be improved by treatment (e.g. with phosphoric acid or a fluorocarbon) of the glass tube

7 H. W. Melville and J. C. Robb, Proc. Roy. Soc., A, 1949,

196, 79. ⁸ J. M. Ditz, C. G. Hill, jun., and R. C. Reid, J. Phys. Chem., 1969, **73,** 1169.

⁹ O. Glemser, U. Hauschild, and G. Lutz, Z. anorg. Chem., 1952, 269, 93.

in the section from E_2 to the cell to prevent surface recombination of hydrogen atoms, but the E_2 to E_3 technique is much more convenient. A further illustration of the E_1 to E_2 versus E_2 to E_3 method is provided by results on BrO_2 : with a blank, cold central caesium iodide window, passage of a $Br_2: O_2$ gas mixture ($Br_2: O_2 \approx 1:5$) through the cell P to Q and striking of a discharge E_2 to E_3 , gave excellent i.r. spectra ¹⁰ due to (BrO_2)_x; repeating with an E_1 to E_2 discharge gives no product on the window. Furthermore, the copper block, except where it was brushed by the hydrogen discharge (where the block was warmed by



FIGURE 3 3-Methylbut-1-ene spectrum at 77 K after reaction with hydrogen atoms (bands due to 2-methylbutane = X)

direct contact with the plasma), appeared bright red when warmed from 77 K to room temperature due to the formation of copper hydride (soluble in pyridine). The important point is that the colour only appeared after the block warmed up since the hydrogen atoms, trapped in the characterised by their known i.r. spectra. These reactions thus provide a useful test of the potential of the technique.

Results.—(a) Figure 3 shows the i.r. spectrum of 3-methylbut-1-ene before and after subjection to a hydrogen discharge. It is clear that spectral changes are due to the formation of 2-methylbutane as expected from Klein and Scheer's work.³ Furthermore, Figure 4 shows the effect of a deuterium discharge which shows spectral changes due to the formation of deuteriated products (the spectra of these products have not been published).

(b) Figure 5 shows the results of similar experiments with *trans*-but-2-ene, where n-butane was found. It is noteworthy that Klein and Scheer observed no reaction ³ between thermal hydrogen atoms and *trans*-but-2-ene at 77 K [although in later studies they obtained reaction with *trans*but-2-ene highly diluted (1%) in propane ¹²]. In the present experiments the reaction may be due to greater reactivity of the discharge produced hydrogen atoms and/or differences in experimental conditions. That small differences in activation energy have a substantial effect at low temperature, as observed by Klein and Scheer, is shown by the lack of reaction of deuterium atoms with *trans*-but-2-ene.

In all the experiments after they had warmed to room temperature an oily material was left on the window. The material had a distinctive smell, weak vibrations in the i.r. region (3 bands between 2850 and 3000 cm⁻¹ and two broad bands at *ca*. 1480 and 1380 cm⁻¹) and a complex mass spectrum. These 'polymers' were probably formed by gasphase reaction by evaporated olefin from the side of the copper block; it is, of course, impossible to confine the olefin to the window alone. The 'polymers' could also be prepared by discharges through gaseous mixtures of hydrocarbon ¹³ and either hydrogen or argon. The 'polymers' were not observed in experiments where hydrogen, deu-



FIGURE 4 3-Methylbut-1-ene spectrum at 77 K before and after reaction with deuterium atoms. X marks new bands (C-D vibrations) or areas of appreciable change in the spectrum. Y marks band due to very small amount of D_2O_{ice} formed by reaction of the cell walls with deuterium atoms

copper ¹¹ at 77 K, will only react with the copper above 77 K. This, apparently irrelevant observation, is germane to experiments where spectral changes were only observed on allowing the window to warm up after the discharge.

The Reaction of Hydrogen Atoms with Solid Olefins

Introduction.—Hydrogen atoms react with solid olefins to give alkanes and other olefins, products that are readily ¹⁰ C. Campbell, Ph.D. Thesis, University of Cambridge, 1966. ¹¹ V. Ponec, Z. Knor, and S. Cerný, J. Catalysis, 1965, **4**, 485. terium, or argon discharges were performed with no reactant on the window. To ensure that hydrogen atoms were reacting with solid olefin, *trans*-but-2-ene was covered by a thick layer of solid carbon dioxide; as above n-butane was formed. Since the carbon dioxide reacted with the hydrogen atoms to form ice obscuring the spectrum at 77 K, the

 R. Kleim and M. D. Scheer, J. Phys. Chem., 1963, 67, 1874.
L. M. Hunter, T. Matsushige, and W. H. Hamill, J. Phys. Chem., 1970, 74, 1883. products were pumped through a trap section, removing the ice, and sprayed onto the window at 77 K.

Discussion.—Before commenting on the above results it is important to establish that the spectral changes really are caused by reaction of hydrogen atoms with the solid olefins in the experiments above, and hence in experiments with other substrates. An alternative explanation is that reaction actually occurs in the gas phase, the olefin being vapourised by the discharge, and the alkane recondensed. This alternative explanation is unlikely because of the results of the experiments with carbon dioxide-covered samples, and because gas-phase reaction would almost certainly yield polymers.

There has been considerable discussion about the mechanism of the reactions of hydrogen atoms with solid olefins.14-18 The results of these kinetic studies have led to very different



FIGURE 5 trans-But-2-ene spectrum at 77 K after reaction with hydrogen atoms (bands due to n-butane = X)

mechanisms, the two principal theories being (i) that the hydrogen atoms diffuse into the solid and react with essentially stationary olefin, and (ii) that the reaction only occurs at the solid surface, the surface alkane produced being continually replaced by diffusion of alkene. Recent work 18 has suggested a mechanism involving a general diffusion model allowing diffusion of hydrogen atoms and all solid components. While our results do not contain the kinetic and other data necessary for a detailed discussion of mechanism, it is clear that hydrogen atoms, at least are capable of diffusion (experiments with carbon dioxide-covered samples), in agreement with other studies.17

The Reaction of Hydrogen Atoms with Solid Hydrogen Cyanide

Introduction.—There have been relatively few ^{1,19} studies of the reactions of hydrogen atoms with inorganic solids at low temperatures, except for the many studies made of reactions with oxygen and ozone.²⁰ The reaction of hydrogen atoms with solid hydrogen cyanide was studied by Geib and Harteck ¹ who reported a product at 77 K which was ' above

¹⁴ M. D. Scheer and R. Kleim, J. Phys. Chem., 1961, 65, 375.
¹⁵ R. Kleim and M. D. Scheer, Preprint. Pap. Intern. Symp.

 Free Rad. (5th) Uppsala, 1961, p. 34.
¹⁶ R. Kleim and M. D. Scheer, J. Phys. Chem., 1962, 66, 2677.
¹⁷ R. L. Espino, J. P. Jones, R. C. Reid, and M. W. P. Strand-berg, J. Phys. Chem., 1968, 72, 3689.
¹⁸ G. C. Rappe, R. C. Reid, and M. W. P. Strandberg, J. Phys.

Chem., 1970, 74, 3176. ¹⁹ V. J. De Carlo and F. O. Rice, J. Phys. Chem., 1961, **65**,

1913.

all, as it appears to the eye, a unified product, ---, and it sat on the wall as a colourless and fairly transparent product.⁴ They reported, on the basis of hydrogen uptake, that ' one comes to a gross compound of the original reaction product which corresponds, more or less exactly, with CNH₃'. This product was found to decompose to give methylamine, hydrogen cyanide, ammonia, and oily products.

Experimental.--In a number of experiments solid HCN was subjected to 45-60 min hydrogen [deuterium] discharges. In each experiment there appeared new i.r. bands at 3200 cm⁻¹ (strong) [2400 cm⁻¹ (medium)], 1600 cm⁻¹ (broad, medium) [1210 cm⁻¹ (weak)], 1110 cm⁻¹ (strong) [D band not seen since it presumably shifts under the strong HCN band at 830 cm⁻¹], and 800 cm⁻¹ (broad, medium weak) [D band too weak and broad to be definitely identified]. The intensities of all these bands were in constant ratio in the various experiments. These experiments involved thick films,²¹ the intensity of the new bands being found to decrease almost entirely for thinner films (this phenomenon will be explained in later work²¹).

As the window was warmed to room temperature and all the volatile products, were pumped off, an 'oily' substance was left on the window. This substance had identical properties to those of the 'polymers' described previously for hydrocarbon reactions. The mass spectrum of the volatile products from hydrogen experiments demonstrated the presence of methane, ethane, propane, probably higher hydrocarbons (impossible to distinguish clearly from the mass spectrometer background), ammonia, and hydrogen cyanide. The i.r. spectrum of the volatile products showed unchanged HCN and appreciable quantities of NH₃, but no trace of methylamine; hydrocarbon bands are not seen because of the low concentration of hydrocarbon present combined with the low extinction coefficient. In deuterium experiments the i.r. spectrum of the volatile products showed bands due to HCN, DCN, NH₃, NH₂D, and NHD₂, these products may have been formed by exchange between HCN and deuteriated NH₃. We prepared ND_3 in our apparatus by passing an N_2 : D_2 mixture through a 1750 V discharge ²²⁻²⁴ for 15 min. The gaseous ND₃ was found to exchange instantly with HCN to give an equilibrium mixture of HCN, DCN, NH₃, NH₂D, NHD₂, and ND₂

Identification of the Infrared Bands Produced at 77 K.-Examination of the position and intensity of the i.r. absorption bands of solid NH₃ and methylamine shows no correlation with bands produced in the present experiments at 77 K. However, since it could be argued that the discharge products are not pure solids but compounds in a matrix of HCN we investigated the spectrum of NH₃ in solid HCN. Although the spectra had several similar bands, detailed consideration showed that the spectra were different.

Discussion.—These experiments show that hydrogen atoms react with solid HCN at 77 K to form an intermediate compound that decomposes as it is warmed to room temperature to form ammonia, methane, ethane, and higher

²⁰ M. Venugopalan and R. A. Jones, Chem. Rev., 1966, 66, 133.

 P. M. A. Sherwood, following paper.
A. K. Brewer and J. W. Westhaver, J. Phys. Chem., 1930, 34, 153.

 K. Stewart, Nature, 1946, 157, 191.
M. Suyuki, S. Takahashi, and S. Miyazoki, J. Chem. Soc. Japan, 1954, 75, 1265 and 1955, 76, 32.

carbons. Identification of the intermediate is difficult because N-H deformation frequencies cover such a wide range of frequencies.

The compound CNH₃ suggested by Geib and Harteck would correspond to the imine H₂C=NH. Imines are, of course, well known organic intermediates, though CH₂=NH has been found too unstable to be detected under ordinary conditions. CH₂=NH is an attractive suggestion since it simply involves addition of hydrogen, a process of low activation energy which is thus favoured under these conditions. Imines²⁵ have been found to have spectra similar to those of secondary amines with extremely weak frequencies in the 1650-1550 cm⁻¹ region (the weak band at 1210 cm^{-1} in the deuterium experiments may be caused by such a deformation). The C=N absorption has been found to occur in this region, e.g. Ph-N=C- has a strong absorption at 1600-1639 cm⁻¹. Thus the intermediate might be $H_2C=NH$ with the following frequencies in the i.r. spectrum:

2500---3500 cm⁻¹ (centre 3200 cm⁻¹) N-H and C-H stretch. (2400 cm⁻¹ in D experiments) 0-11 - - 1 1 37 77

1600 cm ⁻¹	C-N stretch and N-H
	deformation.
(1210 cm^{-1})	N-D deformation.
1110 cm ⁻¹ , 800 cm ⁻¹	N-H deformation.

In the light of the total absence of methylamine at both room temperature and 77 K, Geib and Harteck's decomposition, $2H_3CN \longrightarrow CH_3NH_2 + HCN$ must be discounted. Geib and Harteck also fail to explain how a reasonable

²⁵ L. J. Bellamy, The Infrared Spectra of Complex Organic Molecules, New York, John Wiley, 1958, 2nd edn.

²⁶ C. K. Jen, S. N. Foner, E. L. Cochran, and W. A. Bowers, *Phys. Rev.*, 1958, 112, 1169.
²⁷ S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen,

J. Chem. Phys., 1960, 32, 963.

28 V. B. Kazanskii and G. B. Pariiskii, Proceedings of the 6th International Conference on Free Radicals, Cambridge, 1963.

equation can be constructed to explain their observation of ammonia in the decomposition products.

Hydrogen atoms are capable of being trapped by solids at a variety of temperatures ²⁶⁻³². When the temperature rises reaction can occur between these hydrogen atoms and the solid in which they were trapped. H₂C=NH is consistent with the decomposition products which would be formed by such a process. The decomposition might therefore have the mechanism:

$$H_{2}C=NH + 2H \longrightarrow \cdot CH_{3} + \cdot NH_{2}$$
$$\cdot NH_{2} + H \longrightarrow NH_{3}$$
$$\cdot CH_{3} + H \longrightarrow CH_{4}$$
$$2CH_{3} \longrightarrow C_{2}H_{6}$$
$$C_{2}H_{6} + H \longrightarrow \cdot C_{2}H_{5}$$
$$\cdot C_{2}H_{5} + \cdot CH_{3} \longrightarrow C_{3}H_{8}$$
etc.

which would explain the formation of the volatile decomposition products. It is significant to note that it is difficult to explain the observation of methane in the decomposition products without such a mechanism.

The research was supported by a grant from the S.R.C. One of us (P. M. A. S.) thanks the Salters' Company and Downing College, Cambridge for the award of Fellowships.

[0/2135 Received, December 15th, 1970]

29 V. B. Kazanskii, G. B. Pariiskii, and V. V. Voevodskii, Discuss. Faraday Soc., 1961, **31**, 203. ³⁰ M. A. Long and J. E. Willard, J. Phys. Chem., 1970, **74**,

1207.

- ³¹ P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, p. 84.
- ³² C. J. Ultee and C. R. Kipford, J. Chem. Phys., 1970, 52, 3462.

2478