JOURNAL OF CATALYSIS 49, 356–362 (1977)

Studies of the Surface and Catalytic Properties of Boron Phosphate with Isotopic Molecules

II. The Interaction of Equimolar Mixtures of H_2 and D_2

J. B. Moffat and L. G. Scott

Guelph–Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus,
Department of Chemistry University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

Received February 21, 1977

Approximately equimolar gas phase mixtures of H_2 and D_2 were contacted with boron phosphate at initial total pressures between 128 and 326 Torr and a temperature of 750 K, for times of approximately 10 h. The gas phase concentrations of D_2 were in all cases severely diminished, while those of H_2 suffered relatively small depletions. Absolute rate constants and external orders as calculated from the changes in gas phase D_2 concentration are in reasonable agreement with those measured from experiments in which the gas phase consisted of D_2 only. Losses of up to 2.3×10^{-5} mol/m² of deuterium atoms to the surface were measured. Rideal and Eley mechanisms are consistent with the data.

INTRODUCTION

In the first paper (*1*) (hereafter referred to as I) of this series, the interaction of D_2 with boron phosphate was described. It was found, on contacting D_2 with boron phosphate at temperatures in the range from 425 to 468°C and initial D_2 pressures from 80 to 176 Torr, that HD and H_2 were produced in the gas phase in molar proportions of approximately 2:1, respectively. Further, the rates of change of the moles of D_2 and HD in the gas phase (blank corrected) were found to be linear functions of the moles of D_2 and HD remaining, respectively, and appropriate rate constants were obtained. The use of the differential form of the first-order rate equation circumvented the problem associated with apparent lack of attainment of equilibrium even after 10 h of reaction time. Although direct comparison with data in the literature was not possible because of the lack of detailed kinetic studies of deuterium exchange on oxides, it was pointed out (*1*) that results obtained by Hall *et al.* (*2*) for the Ta–H system gave an activation energy for the exchange process of 14.9 kcal mole^{-1} and rate constants of 5.0×10^{-4} to 2.8×10^{-3} sec^{-1} over a temperature range of 530 to 640°C. The rate constants reported in I ranged from 0.2×10^{-4} to 1.8×10^{-4} sec^{-1}. While no claim was made that any direct relationship exists between the two systems, the results of Hall *et al.* (*2*) compared reasonably well with the values obtained for D_2 over boron phosphate (*1*). Finally, in I, the existence of exchangeable hydrogen atoms on the surface in quantities up to 1.3×10^{-5} mol/m² was demonstrated, and empty sites, that is, sites apparently not previously occupied by hydrogen atoms, were shown to exist in concentrations as high as 1.5×10^{-5} mol/m².

As an extension of our previous work it appeared to be both worthwhile and interesting to examine the effect of including

ISSN 0021-9517

protium (H_2) along with deuterium in the gas mixture contacting the catalyst. Such an addition would provide for the possibility of the H_2–D_2 exchange reaction without precluding the occurrence of those exchange reactions of D_2 with the surface originally examined in paper I. The present paper, therefore, is concerned with the interaction of approximately equimolar mixtures of H_2 and D_2 over the catalyst boron phosphate. The reactions of mixtures of hydrogen and deuterium have been and continue to be studied on a wide variety of solid surfaces. However, no reports of such work on boron phosphate or, for that matter, any of the phosphates, are available.

EXPERIMENTAL METHODS

Materials

As reported in the previous paper (*1*), two different samples of boron phosphate with phosphorus/boron molar ratios of 1.12 and 1.17 were prepared from boric acid (Fisher reagent grade) and orthophosphoric acid (Fisher reagent grade 85%) in a manner similar to that described previously (*3*). The boric acid (particle size less than 20-mesh) was slowly added to the phosphoric acid heated to 40°C in a stirred glass reactor and the temperature was maintained and stirring continued for a 5-h period. The product was dried in air at 150°C for 24 h and subsequently at 360°C for 12 h. The white solid was then ground and sieved to 100-mesh. The two different ratios of boron phosphate are both in the range (1.0 to 1.4) studied previously (*4*) and in which the highest catalytic activity is obtained.

Apparatus and Procedure

The apparatus and method were essentially similar to those outlined earlier (*1*), with analyses of the concentrations of H_2, HD, and D_2 in the reactor system being done by monitoring *m/e* peaks of 2, 3, and 4 in a mass spectrometer attached to the reactor via a variable leak valve. Calibrations were performed with known mixtures and were checked periodically.

Aliquots of the samples of boron phosphate were pretreated in the quartz reactor at 10^{-6} Torr and at the reaction temperature for 13 h. Known approximately equimolar quantities of deuterium and hydrogen were then introduced and the progress of the reaction was followed. Surface areas of the samples were measured both before pretreatment and after reaction. For the catalyst of phosphorus/boron molar ratio of 1.12, the surface areas of aliquots were 15.4 ± 1.0 and 29.5 ± 1.0 m^2/g before pretreatment and after reaction, respectively, while the catalyst of 1.17 P/B ratio had surface areas of 8.5 ± 0.5 and 24.0 ± 1.0 m^2/g, respectively. Separate experiments were performed which showed that the increase in surface area occurred during the pretreatment of the catalyst, with little or no change of area taking place during the reaction itself. Temperatures of approximately 480°C and initial total pressures from 128 to 326 Torr were employed for the reactions. The results from similar experiments performed in the absence of catalyst were employed as corrections to the results obtained in the presence of boron phosphate.

Since the gas phase concentrations of H_2, D_2, and HD were followed with time, the conglomerate effect of exchanges of these molecules with the surface and the H_2–D_2 reaction itself could be measured.

RESULTS AND DISCUSSION

In the previous experiments in which boron phosphate was contacted with D_2 (*1*), the gas phase deuterium (D_2) concentration decreased with time while that of HD and H_2 increased. In the present experiments, as expected, both H_2 and D_2 disappeared from the gas phase during the course of the reaction, while HD was

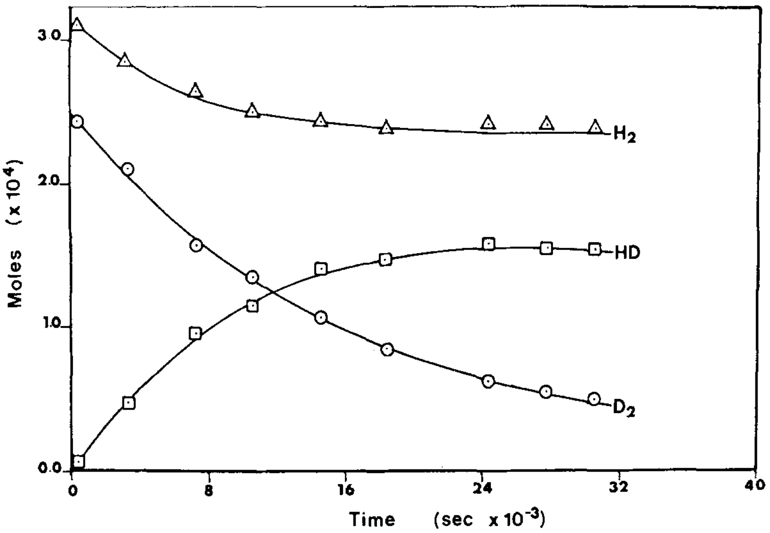

FIG. 1. Variation of the amounts of H_2, D_2, and HD during the interaction of equimolar quantities of H_2 and D_2 with boron phosphate (T = 477°C), $P_{D_2}{}^0 = 86.0$ Torr, $P_{H_2}{}^0 = 82.9$ Torr).

formed (Fig. 1). However, in all cases, the gas phase concentration of D_2 suffered a significantly larger depletion than that of H_2. Further, an amount of HD greater than that of H_2 lost was produced during the course of the approximately 9-h reactions. A number of possible explanations may be given for such observations. While, as suggested previously (*1*), D_2 (and presumably H_2) may chemisorb on empty sites and thus be removed from the gas phase, any H_2 which exchanges with surface hydrogen produces another H_2 molecule and does not reduce the gas phase concentration of H_2. In the case of D_2, its reaction with surface hydrogen is evident in the production of HD, and in the marked decrease in the gas phase concentration of D_2. Further, it is possible that, in the later stages of the reaction, a secondary reaction of H_2 with the increasing quantity of surface deuterium becomes more important, and adds to the production of HD while at the same time reducing the H_2 concentration. In addition, some reverse reaction of HD to give D_2 and H_2 or with surface hydrogen to give H_2 and surface deuterium may occur. These various possibilities are contained within the three reaction pathways which have been suggested (*5–7*) for the exchange of isotopes between the gas phase and a solid catalyst.

$$\left.\begin{aligned} &D_2(g) + H(s) \rightleftarrows HD(g) + D(s) \\ &HD(g) + H(s) \rightleftarrows H_2(g) + D(s) \end{aligned}\right\} (R')$$

$$\left.\begin{aligned} &D_2(g) + 2H(s) \rightleftarrows H_2(g) + 2D(s) \\ &HD(g) + 2H(s) \rightleftarrows H_2(g) \\ &\qquad\qquad + D(s) + H(s) \\ &HD(g) + 2D(s) \rightleftarrows D_2(g) \\ &\qquad\qquad + D(s) + H(s) \end{aligned}\right\} (R'')$$

$$D_2(g) + H_2(g) \rightleftarrows 2HD(g) \quad (R)$$

It was found, in all cases, that the rate of decrease of the concentration of deuterium in the gas phase was proportional to the amount of D_2 remaining in the gas phase (Fig. 2). As pointed out in (*1*), the use of the differential form of the first-order rate equation circumvented the problem associated with apparent lack of attainment of equilibrium. The absolute rate constants thus obtained are shown in column 5 of Table 1. These values are reasonably similar to those obtained previously (*1*) for D_2 over boron phosphate, where reactions

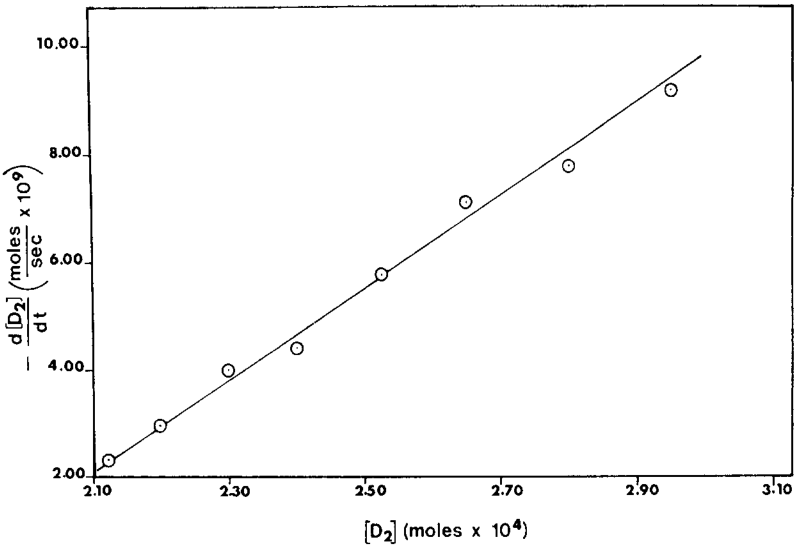

FIG. 2. First-order kinetics from the rate of disappearance of D_2 (same reaction as in Fig. 1).

under similar experimental conditions are compared. For example, the rate constant for D_2 obtained at 753 K and 69.0 Torr was previously given as 2.31×10^{-15} mol·sec^{-1}·m^{-2}, to be compared with a value for D_2 in the present work of 2.02×10^{-15} mol·sec^{-1}·m^{-2} measured at 753 K and 61.7 Torr. An external order of 1.0 (±0.2) was obtained from these data, to be compared with the value 0.8 (±0.2) obtained in a similar calculation for the reaction of D_2 over boron phosphate (*1*).

The near similarity of the rate constants and external orders for the disappearance of D_2 from the gas phase in the two cases, (i) where the gas phase, at least initially, consists entirely of D_2, and (ii) where the gas phase consists of both H_2 and D_2, suggests thst the processes in the two cases are essentially equivalent. This would ap-

TABLE 1

Absolute Rate Constants and Net Amounts of Deuterium Gained by the Surface of Boron Phosphate as Calculated from the Decrease of Gas Phase D_2 Concentration and from the Increase in Gas Phase HD Concentration

Catalyst P/B (mol/mol)	Initial H_2 pressure (Torr)	Initial D_2 pressure (Torr)	Reaction temperature (K)	Rate constant		$[D^*]_{max}$ (mol·m^{-2}) (× 10^5)
				$k_m^{D_2}$(× 10^{15}) (mol·sec^{-1}·m^{-2})	k_m^{HD}(× 10^{15}) (mol·sec^{-1}·m^{-2})	
1.12	62.2	61.7	753	2.02	4.79	0.67
1.12	68.1	67.4	733	1.91	3.78	0.85
1.17	66.3	64.9	753	1.95	4.29	1.19
1.17	163.0	162.6	750	3.64	6.80	2.21
1.17	109.2	104.4	749	3.16	4.44	0.90
1.17	128.3	132.1	749	4.95	5.86	2.28
1.17	64.8	63.8	750	1.48	4.03	1.10
1.17	82.9	86.0	750	3.02	5.11	1.92

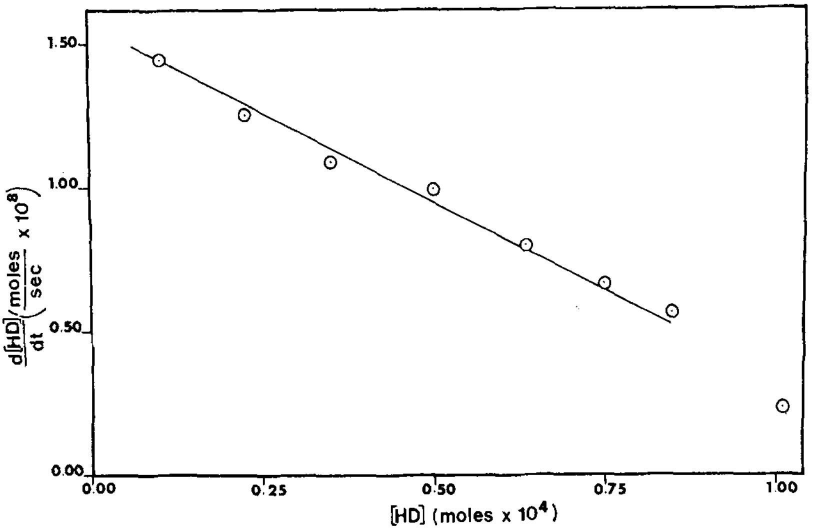

FIG. 3. First-order kinetics from the rate of production of HD (same reaction as in Fig. 1).

pear to render unlikely any significant contribution of a purely gas phase H_2–D_2 reaction. The observation of the substantial differences in the changes of H_2 and D_2 concentrations as the reactions proceeded provides additional support for such a conclusion. Heylen *et al.* (*5*) in their studies of the hydrogen–deuterium equilibration over synthetic faujasites and Kemball and McCosh (*8*) in their work on CoX zeolites have observed the same identity of kinetic parameters for the D_2–surface exchange and the H_2–D_2–surface exchange. These authors have noted that such identities would point to a common slow step for both reactions.

An additional set of rate constants (column 6 of Table 1) was obtained by noting that the rate of formation of HD decreased linearly with the gas phase concentration of HD (Fig. 3). Again, where comparisons are possible, the rates of production of HD in the $H_2 + D_2$ and in the D_2 exchange reactions (*1*) are in reasonable agreement. The external order of the $H_2 + D_2$ reaction determined from the HD rate data was calculated to be 0.6 (±0.1), to be compared with a value of 0.9 (±0.2) found for HD in the previous experiments with D_2.

It is of interest to note that the values of rate constants obtained in the present work fall in the same range as those obtained by Heylen *et al.* (*5*) with synthetic faujasites.

The number of moles of deuterium atoms gained by the surface was calculated from

$$[D^*] = 2[D_2]^0 - (2[D_2]_t + [HD]_t),$$

where $[D_2]^0$ represents the initial gas phase concentration of D_2, and $[D_2]_t$ and $[HD]_t$ are the gas phase concentrations of D_2 and HD at time t. Such values of $[D^*]$ were found to fit the integrated Elovich equation (Fig. 4). It was demonstrated in (*1*) that deuterium is lost from the gas phase to the surface by exchange with surface hydrogen atoms and by occupying sites on the surface not previously occupied by a hydrogen atom. The quantity $[D^*]$ defined above represents the net loss of deuterium atoms from the gas phase, and consequently the quantities calculated refer to the deuterium atoms gained by the surface by the two processes just mentioned. While the latter of these processes may obviously be labeled as a chemisorption process, it is not so obvious that an exchange process should be so labeled. Nevertheless, perhaps as a consequence of the relatively nondiscriminating nature of the Elovich equation, the numbers of deuterium atoms gained by the boron phosphate at various times by whatever process do fit such an equation. Calculated values of the two constants in the Elovich equation as obtained in the present experiments were found to be of the same order of magnitude as those obtained in the earlier D_2 work.

As mentioned above, deuterium atoms may be gained by the surface through exchange with a surface hydrogen or through apparent chemisorption on an empty site, that is, a site not already possessing a hydrogen atom. Consequently, the amount of deuterium gained by the surface ($[D^*]$) is indicative of the total number of exchangeable and empty sites for a given temperature and pressure. The maximum values of deuterium gained by the surface ($[D^*]_{max}$) in a given experiment (column 7 of Table 1) fall in the range 0.7 to 2.3 ($\times 10^{-5}$) mol/m^2, which is approximately the same as that found in the experiments with D_2 on boron phosphate (*1*). In those cases where the $[D^*]$ versus times curves had leveled off, the maximum was taken as this level value, while in some others $[D^*]$ was still increasing slowly, so $[D^*]_{max}$ was taken to be the value at the end of the 8- to 10-h reaction. In addition, it should be pointed out that, as has been mentioned previously, equilibrium with respect to the H_2–D_2 exchange reaction is evidently not attained in the present reactions (nor in the previous D_2 reactions), and since the values of $[D^*]_{max}$ are observed to increase with increasing pressure, the actual number of exchangeable and empty sites available to take up deuterium may well be somewhat higher than that expressed by $[D^*]_{max}$. The results of measurements (*9*) of the oxidation of iodine ions on boron phosphate suggest that approximately 0.3×10^{-5} mol/m^2 of iodine can be chemisorbed on the surface of a sample of boron phosphate with a P/B ratio of 1.22. Further, the total concentrations of acid sites, as measured from titrations of *n*-butylamine, fall between 2×10^{-5} mol/m^2. All three sets of values, representing different measurements of surface sites, show a convincingly similar magnitude. It would not be expected that such values would exactly correspond, since the kinds of sites measured are not identical.

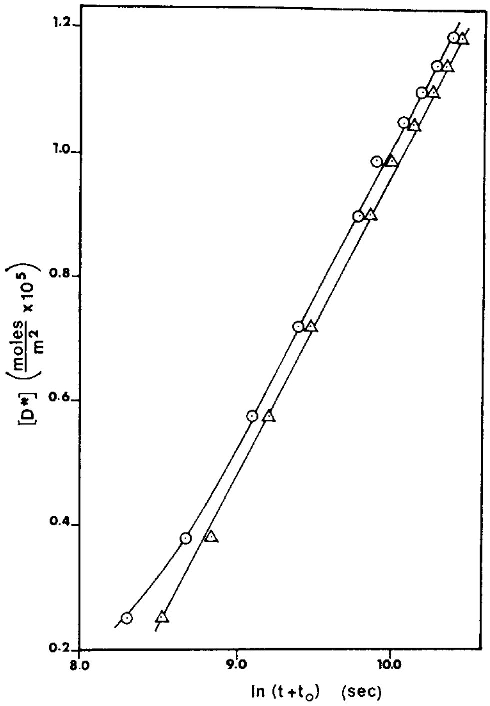

FIG. 4. Elovich plot for the gain of deuterium by boron phosphate. [absicissa is ln t(⊙) or ln $(t + 1000)$ (△)].

It is interesting to examine the applicability of the various possible mechanisms for H_2–D_2 exchange to the present results. One mechanism (*R*) involves the reaction of H_2 and D_2 entirely in the gas phase without participation of the solid surface. However, the results of the present work together with the previous work (*1*) on the exchange of deuterium gas with boron phosphate show that the absolute rate constants for loss of D_2 from the gas phase are, for comparable conditions of temperature and pressure, approximately equal. In addition, the rate constants for D_2 consumption are not, in general, equal to one-half of those for HD production which they presumably should be for an entirely gas phase reaction. Further, a net loss of deuterium atoms from the gas phase occurred in the H_2–D_2 exchange experiments on boron phosphate. Consequently, an entirely gas phase mechanism can be ruled out in the present work.

The results of the previous work on D_2 exchange with the surface of boron phosphate provide evidence for both the exchange of deuterium atoms with surface hydrogen as well as the occupancy of empty sites by deuterium. The latter observation could be interpreted as favoring either a Bonhoeffer–Farkas or Rideal mechanism. However, the observation, with both D_2 and H_2–D_2 experiments, that the absolute rate constants increase with increasing pressure, implies the operation of an Eley mechanism, and plots of the data in the form of $1/k_m$ versus $1/(P)^{\frac{1}{2}}$ for both D_2 and HD data, although displaying scatter, are sufficiently linear to provide further support for the Eley mechanism (*10*). However, since it has been pointed out (*10*) that, for sufficiently low pressures, the rate constant in the Rideal mechanism increases and passes through a maximum as pressure increases, it may not be possible to eliminate the Rideal mechanism in the present case.

It is difficult to explain the deviation of $k_m^{\mathrm{HD}}/k_m^{\mathrm{D_2}}$ from a value of 2 on the basis of either the Eley or the Rideal mechanism. The differences appear to be sufficiently large to support the contention that they are real and not the result of experimental error. An approximate, inverse correlation can be noted between this ratio of rate constants and $[\mathrm{D}^*]_{\max}$, the total number of deuterium atoms taken up by the surface. This could be interpreted as reflecting an increase in $k_m^{\mathrm{D_2}}$ as the number of empty sites available to take up deuterium increases.

The external order, as measured from both the D_2 and HD data, is probably best stated as falling in the range of 0.6 to 1.2. This is consistent with an Eley mechanism at lower coverage or a Rideal mechanism at somewhat higher coverage.

ACKNOWLEDGMENTS

The financial support of the National Research Council of Canada in the form of an operating grant (J. B. M.) and an NRC scholarship (L. G. S.) is gratefully acknowledged.

REFERENCES

1. Moffat, J. B., and Scott, L. G., *J. Catal.* **45**, 310 (1976).
2. Hall, W. K., Wallace, W. E., and Cheselske, F. J., *J. Phys. Chem.* **65**, 128 (1961).
3. Goltz, H. L., and Moffat, J. B., *J. Catal.* **22**, 85 (1971).
4. Moffat, J. B., and Riggs, A. S., *J. Catal.* **42**, 388 (1976), and references contained therein.
5. Heylen, C. F., Jacobs, P. A., and Uytterhoeven, J. B., *J. Catal.* **43**, 99 (1976).
6. Klier, K., Novakova, J., and Jirů, P., *J. Catal.* **2**, 479 (1963).
7. Tsuchiya, S., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **22**, 280 (1971).
8. Kemball, C., and McCosh, R., *Proc. Roy. Soc. Ser. A* **321**, 249 (1971).
9. Moffat, J. B., and Chao, E. *J. Catal.* **46**, 151 (1977).
10. Richard, S., Gravelle, P. C., and Teichner, S. J., *Bull. Soc. Chim. France* 2899 (1973).