dependent only upon the separation of the interacting groups and do not exhibit the angular features established in the present paper. In any case, the shielding of these fields results from a distortion of the hydrogen orbital and is therefore described by the E^2 term in eq 7 which is generally small.

The linear variation of $\delta_E{}^H$ with E_z seems to parallel the dependence of $\delta_s{}^H$ on the component of the steric force in the bond direction. Both effects are best explained by changes in the Lamb shielding of the proton resulting from removal of electronic charge from the hydrogen orbital.[21] Since van der Waals and electric field shifts appear to be based upon a common mechanism, it is interesting to speculate that significant nonrandom fields can be produced in otherwise nonpolar groups when they are in close steric contact.

Conclusion

The magnetic deshielding experienced by a spatially crowded hydrogen, H, has been related to the conformational geometry existing between the H–C bond and the interacting hydrogen, H′. Specifically, $\delta_s{}^H$ was shown to depend upon the component of the nonbonded H′H repulsive force along the H–C internuclear axis. As an explanation for this effect, a model involving sterically induced charge polarization in the H–C bond has been proposed. A semiempirical argument was given to demonstrate that the model is capable of explaining both the proton and C^{13} steric shifts which result from the van der Waals repulsions between proximate hydrogens.

Since the magnitude of the proton steric shift is intricately related to the molecular geometry, it is expected that eq 6 will find important applications in molecular structure studies using nmr techniques. The relationship points out the need for additional theoretical work on the effects of nonbonded interactions between proximate groups in a molecule. It would also be of interest to investigate the steric effects induced by atoms or groups other than hydrogen.

Acknowledgment. Dr. D. J. Duchamp carried out the refinement of the crystallographic data for 3,4-benzophenanthrene and provided the Waser program used to obtain the atomic coordinates for type-VI structures. For these services, the author wishes to express appreciation.

Isotope Exchange Rates. VI. The Homogeneous Self-Exchange in Hydrogen Deuteride

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Abstract: The isotopic exchange reaction $2HD \rightarrow H_2 + D_2$ was studied in a single-pulse shock tube over the temperature range 1120–1659°K. Sample mixtures consisted of 1.0–4.5% HD in argon. The total density behind the reflected shocks ranged from 1×10^{-2} to 7×10^{-2} mol/l. High-temperature residence times were about 1 msec. The deduced power rate expression is 1.43 ± 0.1 order in HD and 0.57 ± 0.1 order in argon. The second-order rate constant for the reaction is $k_s = 2.45 \times 10^9 \exp[(-35{,}940 \pm 2000)/RT]$ l. mole^{-1} sec^{-1}. These data support a mechanism similar to that proposed for other exchange reactions [$D_2 + H_2$, H_2S, H_3N, H_4C]. In this model, the probability for exchange during a collision of two HD molecules is greatly enhanced when one of them is excited to or above a critical vibrational level so that the over-all exchange rate is limited by the rate of repopulating that level (the third for HD). The ratios of the relative excitation efficiencies of HD–HD and HD–Ar collisions and the relative probabilities for exchange in HD*–HD collisions *vs.* deexcitation *via* HD*–Ar collisions have been determined from the rates measured in these experiments. Also, an over-all rate constant for vibrational excitation of HD by argon was obtained. These kinetic parameters are entirely compatible with related parameters previously reported for the reverse of this exchange reaction, $H_2 + D_2 \rightarrow 2HD$, and with data obtained from direct measurement of vibrational relaxation times.

Within the past few years, in shock-tube laboratories at Cornell University and elsewhere, the kinetics of homogeneous bimolecular isotopic exchange reactions in the gas phase at high temperatures have been investigated under a variety of conditions. Most but not all the H/D exchange processes fit a single pattern, wherein the total reaction order of two is partitioned between the reactants and the argon diluent (95–99% of the mixture). The argon order was found to range from 0.5 to 0.7. Typical of these reactions are the exchanges between D_2 and H_2,[1] D_2 and H_2S,[2] D_2 and NH_3,[3] D_2 and CH_4,[4] and $^{15}N_2$ and $^{14}N_2$.[5] The observed power rate expressions, the magnitudes of the rates of product formation, and their dependence on reaction temperature led to the conclusion that under these shock-tube conditions the reactions do not occur *via* hard bimolecular collisions which pass through four-center transition states, nor *via* free-radical processes. However, the data are consistent with the assumption that reaction occurs only when one of the colliding

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species contains a minimum amount of vibrational excitation, so that the transition state is a vibrationally excited intermediate. The rate-limiting process is the rate of repopulating the critical vibrational level, and it appears that the transition probability for reaction depends on which of the reacting partners contains the necessary vibrational energy. In two of these investigations[1a,5] the preexponential factors for the exchange rate were calculated from vibrational relaxation data obtained in independent experiments, and these compared favorably with the experimentally determined values. In several cases, estimates of the relative rates of excitation by the various species present, according to the vibrational excitation mechanism, proved to be in good agreement with independently reported vibrational relaxation data.

One of the strongest tests for a given mechanism is the experimental demonstration that the magnitudes of the reverse reaction rate constants obtained in mixtures which consist mostly of products are compatible (*via* the known equilibrium constants) with the forward reaction rate constants obtained under conditions where the mixture consists mostly of reactants. The purpose of this investigation was to test the vibrational excitation mechanism in this manner. It will be shown that the data obtained are indeed consistent with the proposed mechanism in general, and specifically with the previously published data on the $H_2 + D_2$ reaction. A discussion of other possible mechanisms and of the observations which tend to contradict them will also be given.

Experimental Section

The single-pulse shock tube used in this investigation was made of 1 in. i.d. Pyrex tubing. The end block and other fittings are brass. The length of the driven section is about 6 ft, and that of the driver (adjustable for tuning) is about 3 ft. This shock tube has been only slightly modified since its use for the $H_2 + D_2$ exchange experiments reported earlier; details of the shock-tube dimensions and associated electronic circuitry may be found in that report.[1a] The test section was pumped to a pressure less than 10^{-4} torr (leak and out-gassing rates were less than 3×10^{-4} torr/min) before being filled with sample, and the shock was initiated within 1 min after filling. Immediately prior to and directly after initiation of the shock, 25-cc samples of gas were withdrawn from the downstream end of the shock tube for subsequent mass spectrometric analysis. Series of 20–30 shocks were run on each of 3 days, on mixtures containing 1.0 or 4.5% HD in argon. Temperatures behind reflected shocks were varied from 1120 to 1659°K; total reaction densities ranged from 1.0×10^{-2} to 7.0×10^{-2} mole/l. The experimental conditions for the various groups of runs which yielded data considered to be reliable are summarized in Table I.

Table I. Summary of Experimental Conditions

Mixture[a]	% HD	T_5 range, °K	P_1 range, cm	No. of expts
1A	4.5	1120–1444	3.50–6.60	9
2A	4.5	1202–1640	2.76–4.52	11
2B	1.0	1190–1498	11.80–19.90	10
2C	1.0	1455–1600	3.00–3.56	6
3A	4.5	1232–1659	2.86–4.56	7
3B	1.0	1202–1520	11.15–18.05	7
3C	1.0	1394–1600	2.90–4.02	10
3D	4.5	1211–1436	11.94–16.92	6

[a] The number represents the day; the letter designates the group.

The stock HD sample, obtained from Merck Sharp and Dohme, Ltd., was found to be ≈98% pure (impurities <1% H_2, ≈0.2% D_2, ≈1% air). We did not attempt further isotopic purification. However, the N_2 and O_2 were removed by adsorption on activated carbon, as described below. The carbon was degassed at ≥400°. It was then cooled by liquid N_2 and the impure HD introduced and adsorbed. After many hours (10–16) the charcoal was warmed gradually. The first 80% of the evolved gas was retained. Analysis of this sample showed no detectable traces of N_2 or O_2, and that no measurable exchange of HD had occurred on the carbon. (Additional details of the purification process are given in the Appendix.) The argon diluent, Airco 99.998%, was used as obtained from the tanks. The driver gas was helium. Samples of HD in argon were allowed to mix for several days before use; that complete mixing had occurred was verified by mass spectrometric analysis of unshocked reference samples.

Mylar diaphragms were used for the first groups of experiments, 1A and 1B. The data from the high-density runs (1B) were discarded and are not included in Table I, because subsequent analysis of the reaction products showed them to be contaminated by small amounts of helium. This indicated that a significant amount of mixing had occurred during the dwell time or cooling process or both. Thereafter, aluminum was used for the diaphragm material and no further mixing of driver gas was detected in the shock-heated samples.

Samples taken from the shock tube were analyzed for HD, D_2, Ar, O_2, and N_2 (and some also for H_2O) on a C.E.C. Model 21-103 mass spectrometer. Since earlier studies had indicated that "burping" of light species (*i.e.*, H_2, HD, D_2) occurs when a Vacion pump is used to pump mixtures of these light gases and relatively heavier species such as argon, an oil diffusion pump, isolated by a liquid nitrogen cooled trap, was used to pump the ion source of the mass spectrometer. Relative sensitivites of the instrument for HD and D_2 were determined by analyzing samples containing 1% of each of the pure species in argon.

The high-temperature dwell time was estimated for each experiment from the duration of the high-pressure pulse produced by the reflected shock (sensed by a Kistler piezoelectric gauge located near the end of the shock tube at the point from which the 25-ml sample was taken for analysis). No corrections were made for additional reaction (<10% of total) which takes place during the quenching process.

Reduction of the Data

A. The Power Rate Expression. A total of 66 sets of data were obtained from the eight valid groups of single-pulse shock-tube experiments run under the conditions listed in Table I. First the data were reduced to fit a power rate expression of the form (initial rate only)

$$\mathrm{d}[D_2]/\mathrm{d}t = k_p[\mathrm{Ar}]^x[\mathrm{HD}]^y \qquad (1)$$

Since $K_{eq} = {}^1/_4$ for the exchange step at shock temperatures, and since the extents of reaction were large at the higher temperatures and densities, the back reaction had to be taken into account. Equation 1 was rewritten in the approximate form

$$\frac{\mathrm{d}[D_2]}{\mathrm{d}t} = k_s[\mathrm{Ar}]^x[\mathrm{HD}]_0^{y-1}\frac{[D_2]_{eq} - [D_2]}{[D_2]_{eq}}[\mathrm{HD}]_0 \qquad (2)$$

where $k_s \approx k_p$. Integration leads to

$$k_m t = -\frac{[D_2]_{eq}}{[\mathrm{HD}]_0} \times \ln\left\{\left[1 - \frac{[D_2]_t\,[\mathrm{HD}]_0}{[\mathrm{HD}]_0\,[D_2]_{eq}}\right]\Big/\left[1 - \frac{[D_2]_0\,[\mathrm{HD}]_0}{[\mathrm{HD}]_0[D_2]_{eq}}\right]\right\} \qquad (3)$$

where k_m is a pseudo-first-order rate constant with respect to $[\mathrm{HD}]_0$, defined by

$$k_m = k_s[\mathrm{Ar}]^x[\mathrm{HD}]_0^{y-1}$$

However, since $[D_2]_{eq} = {}^1/_4[\mathrm{HD}]_0$, and $[\mathrm{HD}]_t + 2[D_2]_t = [\mathrm{HD}]_0$

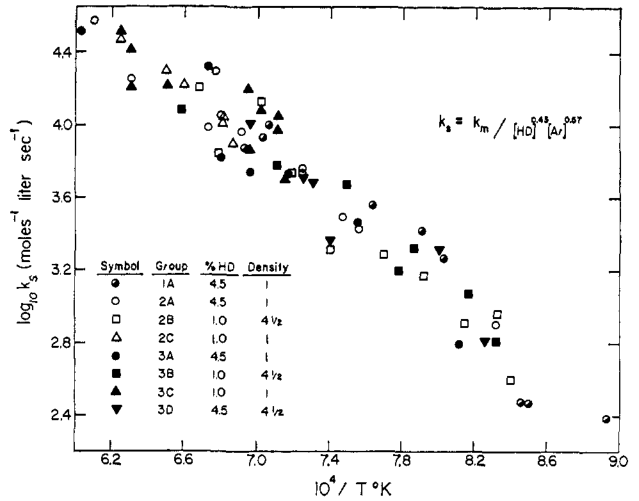

Figure 1. All 66 experimental points plotted on the basis of empirical power rate equation (5).

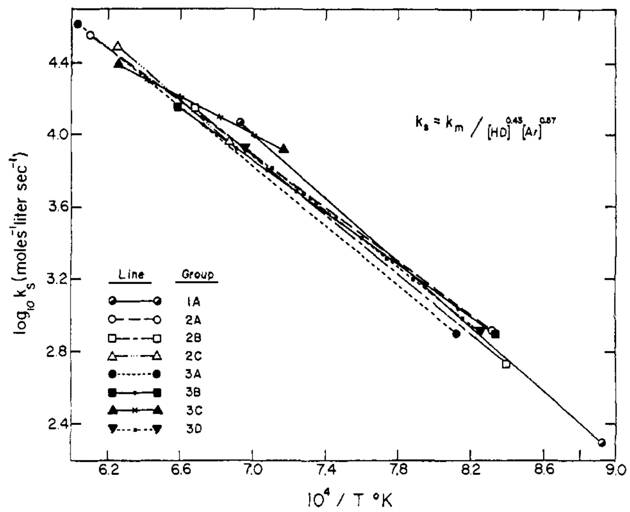

Figure 2. Least-squares lines through individual groups of the data as plotted in Figure 1.

$$k_m t = -\frac{1}{4} \times \ln\left\{\left[1 - \frac{4[D_2]_t}{[HD]_t + 2[D_2]_t}\right]\Big/\left[1 - \frac{4[D_2]_0}{[HD]_t + 2[D_2]_t}\right]\right\} \qquad (4)$$

The magnitudes of k_m were thus computed from the mass spectrometrically measured D_2/HD ratios, and values of log k_m were plotted *vs.* $1/T$. Parallel straight lines were drawn through the separate groups of data. The separation (Δ log k_m) of the lines at a given temperature (1430°K) permits deduction of the reaction orders with respect to HD, argon, and the total density. These results have been summarized in Table II. Only groups of data collected on the same day were used in each comparison, as we believe that this restriction helps to minimize the effects of systematic errors due to differences in shock-tube operation, diaphragm aging, or other imponderables which might affect the data differently on different days.

Table II. Results of Graphical Analyses in Which the Various Groups of Data Were Separately Reduced to Obtain Reaction Orders[a]

Combination	Parameter	Result	Average	Weighted value
2B–2A	x	0.42–0.48	0.48–0.53	0.54
3B–3A	x	0.53–0.57		
2A–2C	$y - 1$	0.46–0.50	0.41–0.44	0.46
3D–3B	$y - 1$	0.50–0.54		
3A–3C	$y - 1$	0.27–0.29		
2B–2C	$x + y - 1$	0.87–0.95	0.90–0.97	1.00
3B–3C	$x + y - 1$	0.80–0.86		
3D–3A	$x + y - 1$	1.03–1.11		

[a] Values in the last column are weighted to give a total order of $(x + y) = 2.0$.

On the basis of these graphical calculations, the reaction was found to have a total order of 2.0 ± 0.1. The corresponding partial orders (weighted to give total order = 2.0) are $y = 1.46 \pm 0.10$ for HD and $x = 0.54 \pm 0.10$ for argon. However, in deducing these parameters, data from group 1A were not used because the second group of data collected on that day had to be discarded. To take this set of data into consideration and to check the general consistency of the data, the best values for x and y for all 66 runs treated together were estimated *via* a multiple regression computer program. The values obtained were $y = 1.40 \pm 0.06$ and $x = 0.56 \pm 0.08$, for a total order of 1.96. On adjusting these to total order 2.0, one obtains $y = 1.43 \pm 0.06$, $x = 0.57 \pm 0.08$, well within the limits of error of the values determined graphically. Hence we believe that the reaction is adequately described by the power rate expression

$$k_m = k_s[Ar]^{0.57 \pm 0.10}[HD]^{0.43 \pm 0.10} \qquad (5)$$

Values for the second-order rate constant k_s were computed from eq 5. The least-squares line through an Arrhenius plot of log k_s *vs.* $1/T$ (see Figure 1) gave

$$k_s = 2.45 \times 10^9 \times \exp[(-35{,}950 \pm 2000)/RT] \text{ l. mole}^{-1} \text{ sec}^{-1} \qquad (6)$$

To check the consistency of the data collected on different days, least-squares lines were calculated separately for Arrhenius plots of each group of data. The resulting lines, shown in Figure 2, are well mixed. This indicates that the data are consistent and well represented by eq 5. The values of the activation energy for k_s deduced from each group of data are given in Table III; the average is 35.08 kcal/mole. However, the value for group 3C is lower than the rest by a wide margin. If that one is deleted, E_a = 36.67 kcal/mole. Since we question the validity of the low value obtained for group C, but have no justification for rejecting that datum, the magnitude of E_a = 35.95 kcal/mole as given in eq 6 represents a fair compromise.

B. Interpretation of the Power Rate Expression. Since the power rate expression (eq 5) is similar to those obtained by Bauer and Ossa[1a] and by Burcat and Lifshitz[1b] for the reverse exchange process, it is justifiable to treat the data according to the vibrational excitation mechanism proposed for such an exchange reaction.

For simplicity consider a two-level model wherein HD is considered to be either in an unreactive state with

Table III. Activation Energies for k_s Deduced from the Eight Groups of Data

Group	E_a, kcal/mole
1A	40.43
2A	33.62
2B	37.39
2C	39.42
3A	37.56
3B	32.32
3C	24.01
3D	35.92
Average	35.08
Average, omitting group 3C	36.67

vibrational energy below the "critical" level, or in an excited state, containing the "critical" energy (or more), so that exchange occurs readily when it collides with *any* other HD molecule, regardless of the degree of excitation of the latter or the relative kinetic energies of the colliders. The excitation process by which HD attains the critical condition in a series of collisions is treated as a single step. This model is expressed by

$$\mathrm{HD} + \mathrm{M}_j \underset{\varkappa_{-\epsilon j}}{\overset{\varkappa_{\epsilon j}}{\rightleftarrows}} \mathrm{HD}^{(\mathrm{v})} + \mathrm{M}_j \qquad (7)$$

$$\mathrm{HD}^{(\mathrm{v})} + \mathrm{HD} \underset{\varkappa_{-x}}{\overset{\varkappa_x}{\rightleftarrows}} \mathrm{H}_2 + \mathrm{D}_2^{(\mathrm{v})} \qquad (8)$$

where j = 1 (Ar) and 2 (HD). (The products $H_2^{(v)}$ + D_2 do appear, but with smaller relative probability.) Considering low extents of conversion, such that the reverse of (8) may be neglected, a steady-state value for $[HD]^{(v)}$ is

$$[\mathrm{HD}^{(\mathrm{v})}]_{\mathrm{ss}} = \sum_j \varkappa_{\epsilon j}[\mathrm{HD}][\mathrm{M}_j] / \left(\sum_j \varkappa_{-\epsilon j}[\mathrm{M}_j] + \varkappa_x[\mathrm{HD}]\right) \qquad (9)$$

Define

$$\alpha \equiv \varkappa_x/\varkappa_{-\epsilon 1}\ [= \varkappa_x/\varkappa_{-\epsilon 1(\mathrm{HD}\leftarrow\mathrm{Ar})}]$$

$$r \equiv [\mathrm{HD}]/[\mathrm{Ar}]$$

$$\gamma \equiv \varkappa_{\epsilon 2(\mathrm{HD}\leftarrow\mathrm{HD})}/\varkappa_{\epsilon 1(\mathrm{HD}\leftarrow\mathrm{Ar})}\ [= \varkappa_{-\epsilon 2}/\varkappa_{-\epsilon 1}]$$

$$\mathrm{rate} \equiv \frac{\Delta[\mathrm{D}_2]}{\Delta t}\left[= \frac{\Delta[\mathrm{H}_2]}{\Delta t}\right]$$

then

$$\mathrm{rate} = \varkappa_x[\mathrm{HD}^{(\mathrm{v})}]_{\mathrm{ss}}[\mathrm{HD}]$$

$$\mathrm{rate} = \varkappa_{\epsilon 1}[\mathrm{HD}][\mathrm{Ar}]\frac{1 + \gamma r}{1 + (1/\alpha)[(1/r) + \gamma]} \qquad (10)$$

At low extents of conversion, rate ≈ $k_m[HD]_0$, and, at high temperatures, $K_{eq} = {}^1/_4$ for the exchange step ($\varkappa_x/\varkappa_{-x}$). Substitution of $k_m[HD]_0$ for "rate" in (10) allows for the reverse reaction, to a good approximation. This leads to eq 11, which is not restricted to low extents of conversion.

$$k_{\mathrm{m}} \approx \varkappa_{\epsilon 1}[\mathrm{Ar}]\frac{1 + \gamma r}{1 + (1/\alpha)[(1/r) + \gamma]} \qquad (11)$$

Empirical values for α and γ were determined by calculating the magnitudes of $\varkappa_{\epsilon 1}$ for many trial combinations of these parameters. For each combination, points on a plot of log $(\varkappa_{\epsilon 1}T^{-1/2})$ *vs.* $1/T$°K were fitted by least squares, and the standard deviations of log $(\varkappa_{\epsilon 1}T^{-1/2})$ values about the best line were obtained. However, a unique combination of α and γ could not be found. The combinations $\alpha = 10^2$, $\gamma = 5$ and $\alpha = 10^3$, $\gamma = 25$ produced comparable small standard deviations; for any α between 10^2 and 10^3 and for corresponding γ's between 5 and 25, combinations could be found which gave equally good fits. The lowest standard deviations obtained by this trial-and-error method were at least as good as those given for k_s *via* the computer optimization of the power rate expression. In an attempt to determine a "best" α, γ combination, least-squares lines were drawn through log $(\varkappa_{\epsilon 1}T^{-1/2})$ *vs.* $1/T$ points for each separate group of data, for each of the combinations tested. But as the lines appeared about equally well converged for the combinations $\alpha = 10^2$, $\gamma = 5$ and $\alpha = 10^3$, $\gamma = 25$, and for some in between, none in this range could be rejected. On the basis of these data alone, we are left with large uncertainties for the values of α and γ.

On looking beyond empirical data fitting, a number of reasons may be offered for favoring the values $\alpha = 100$, $\gamma = 5$ as being more realistic than those at the other end of the acceptable range. First, in most of the isotopic exchange reactions studied in which D_2 was a reactant and which appeared to follow a mechanism similar to that proposed here, values for the ratio $k_\epsilon(D_2 \leftarrow D_2)/k_\epsilon(D_2 \leftarrow Ar)$ (analogous to γ in this study) have ranged from 1 to 5. The only exception appeared in the case of $D_2 + CH_4$[4] where this parameter was reported by us to have a value of ≈100. However, a reassessment of these data has uncovered some inconsistencies which have prompted us to accept a value on the order of 10. Second, while the vibrational relaxation of HD in argon has not been studied, values of 6.8[6] and 4.8[7] have been obtained for the ratio ($D_2 \leftarrow D_2/D_2 \leftarrow Ar$). Vibrational relaxation time measurements essentially give the rate constants for the $1 \rightarrow 0$ transition, whereas the γ values deduced in these exchange studies correspond to transitions at $5 \rightarrow 4$, $4 \rightarrow 3$, or $3 \rightarrow 2$ levels of D_2, HD, and H_2, depending upon the particular reaction. Nevertheless, the ratios ($D_2 \leftarrow D_2/D_2 \leftarrow Ar$), etc. given by the two methods should be similar. Third, a critical comparison of these data with data for the reverse reaction suggests a value of γ = 5–15, as will be shown later in this report. Figure 3 is a plot of the least-squares lines through log $(\varkappa_{\epsilon 1}T^{-1/2})$ *vs.* $1/T$ points for each individual mixture, as was shown in Figure 2 for the power rate representation. Here $\varkappa_{\epsilon 1}$ values were computed from eq 11 with $\alpha = 125$ and $\gamma = 7$. The least-squares line through the totality of the data gives $\varkappa_{\epsilon 1} = 1.90 \times 10^7 T^{1/2} \exp[(-34{,}520 \pm 2000)/RT]$ (where the units for calculating $\varkappa_{\epsilon 1}$ are mole, liter, second).

Consideration of Other Mechanisms

The form of the empirical power rate expression gives a clear indication that this isotopic exchange reaction is not rate limited by the formation of a four-centered transition state during a direct collision between two HD's. The activation energy is about two-thirds of the ≈60-kcal/mole value which rough quantum mechanical calculations suggest for such a mechanism.[8a]

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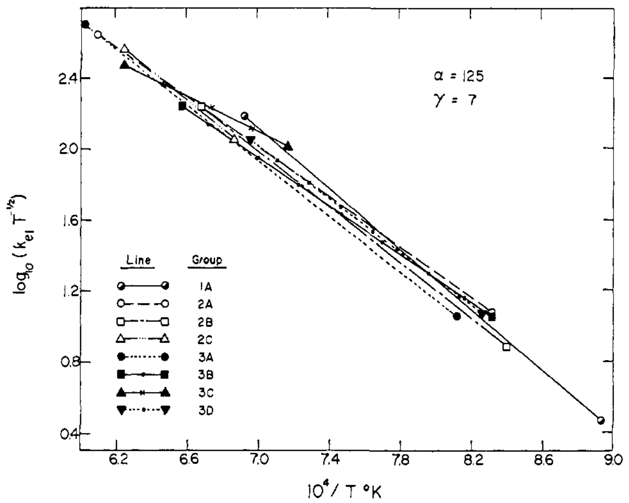

Figure 3. Least-squares lines through individual groups of data plotted on the basis of eq 11 with $\alpha = 125$, $\gamma = 7$. Units for calculation of $\kappa_{\epsilon l}$ are mole, liter, second ($k_{\epsilon l}$ in this figure corresponds to $\kappa_{\epsilon l}$ of the text).

Furthermore, the occurrence of a nonzero order for argon necessitates the inclusion of argon as a partner in the rate-limiting step of any proposed mechanism, but this is not compatible with a model based on bimolecular collisions between reacting molecules, such as postulated by Karplus, *et al.*[8a] Their calculations indicate that, while vibrational excitation of the diatomic colliders greatly enhances the probability for atom exchange, that increment is not sufficient to compensate for the decrease in the populations of vibrationally excited levels due to the Boltzmann factor. The conclusion derived from these classical trajectory calculations is that the major portion of the exchange reaction is due to hard collisions between molecules in their ground vibrational states. Besides being at variance with the many shock-tube experiments cited in the introduction, this conclusion is contradicted by molecular beam experiments between vibrationally cold but rapidly translating beams of HI impinging on DI. As reported by S. B. Jaffe and J. B. Anderson,[8b] no significant amount of HD was generated by the hard collisions.

Finally, it is difficult to devise a free-radical mechanism which plausibly accounts for the dependence of the exchange rate on the argon concentration. From shock-tube measurements of the rate of fragmentation of H_2 in argon,[9] it can be concluded that atom displacement chains caused by HD dissociation could not have contributed significantly to the net conversion. Also, preliminary calculations indicate that radical chains generated by $HD + O_2$ combustion, assuming the maximum possible O_2 concentration, cannot account for the products. However, the chief basis for rejecting a contamination induced free-radical mechanism for this reaction is empirical. A series of experiments was run in which mixtures of 1 and 3% of the unpurified HD in argon were shock heated to 1090–1275°K. Rates of D_2 production were observed which were from 10 to 50 times larger than the rates determined for the purified HD, run under similar conditions. The data obtained in our laboratory with the unpurified HD agree quantitatively with a large amount of data collected by Lifshitz and Burcat,[10] using HD directly as received from M.S.D., Ltd. Furthermore, they found a different rate expression (one and one-half order in HD and zero order in argon) and a higher activation energy (by at least 10 kcal/mole) than we have reported here for clean HD. We believe this to be strong evidence that the presence of oxygen of the order of 10^{-2}% in the reaction mixture forces the exchange reaction to follow a free-radical path, initiated by $HD + O_2 \rightarrow HO + DO$. On the other hand, in the absence of sufficient oxygen and of hot walls to provide sites for atom production, the molecular mechanism dominates.

Comparison with Results for $H_2 + D_2 \rightarrow 2HD$

The empirically deduced power rate expressions reported in two independent studies of the $(H_2 + D_2)$ exchange are similar to eq 5. Bauer and Ossa's data[1a] gave the exponents: 0.38 for H_2, 0.66 for D_2, and 0.98 for argon. The sum of the H_2 and D_2 orders, 1.04, is low compared to the 1.43 for HD, and their argon order is higher by the same margin. Burcat and Lifshitz[1b] reported a total order of 1.3 ± 0.1 for $(H_2 + D_2)$ and an argon order of 0.65 ± 0.1, in agreement with eq 5. That similar mechanisms account for the kinetics of the system $H_2 + D_2 \rightleftarrows 2HD$, proceeding from either extreme of disequilibrium, consistent with the vibration–excitation mechanism, is demonstrated below.

The proposed mechanism, again using the simplified two-level model for the excited species in the complete system, wherein H_2, D_2, HD, and Ar may all be present, is described by eq 12–16, where *i* and *j* designate the

$$H_2 + M_i \underset{k_{-\epsilon i}}{\overset{k_{\epsilon i}}{\rightleftarrows}} H_2^{(v)} + M_i \qquad (12)$$

$$D_2 + M_i \underset{k'_{-\epsilon i}}{\overset{k'_{\epsilon i}}{\rightleftarrows}} D_2^{(v)} + M_i \qquad (13)$$

$$H_2^{(v)} + D_2 \underset{k_{-x}}{\overset{k_x}{\rightleftarrows}} HD^{(v)} + HD \qquad (14)$$

$$D_2^{(v)} + H_2 \underset{k'_{-x}}{\overset{k'_x}{\rightleftarrows}} HD^{(v)} + HD \qquad (15)$$

$$HD^{(v)} + M_j \underset{\kappa_{\epsilon j}}{\overset{\kappa_{-\epsilon j}}{\rightleftarrows}} HD + M_j \qquad (16)$$

various partners which each species may encounter. The notation in eq 12–16 is consistent with that introduced earlier in this manuscript, except that eq 8 has been explicitly disected into its two parts, (14) and (15). Thus

$$\kappa_x\ (8) = k_{-x} + k'_{-x}\ \text{(of 14 and 15)}$$

$$\kappa_{-x}\ (8) = k_x + k'_x\ \text{(of 14 and 15)}$$

In the above, while the superscript (v) denotes each species excited to (or above) its critical vibrational level, one should not assume that this level must be the same for all of them. The steady-state concentrations of these species are

$$[H_2^{(v)}]_{ss} = \frac{\sum_i k_{\epsilon i}[M_i][H_2] + k_{-x}[HD][HD^{(v)}]}{\sum_i k_{-\epsilon i}[M_i] + k_x[D_2]} \qquad (17)$$

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(9) W. Watt and A. Myerson, 6th International Shock Tube Symposium, 1967.

(10) A. Lifshitz and A. Burcat, private communication.

$$[\mathrm{D_2}^{(\mathrm{v})}]_{\mathrm{ss}} = \frac{\sum\limits_i k'_{\epsilon i}[\mathrm{M}_i][\mathrm{D_2}] + k'_{-x}[\mathrm{HD}][\mathrm{HD}^{(\mathrm{v})}]}{\sum\limits_i k'_{-\epsilon i}[\mathrm{M}_i] + k'_x[\mathrm{H_2}]} \tag{18}$$

$$[\mathrm{HD}^{(\mathrm{v})}]_{\mathrm{ss}} = \frac{\sum\limits_j \varkappa_{\epsilon j}[\mathrm{M}_j][\mathrm{HD}] + k_x[\mathrm{D_2}][\mathrm{H_2}^{(\mathrm{v})}] + k'_x[\mathrm{H_2}][\mathrm{D_2}^{(\mathrm{v})}]}{\sum\limits_j \varkappa_{-\epsilon j}[\mathrm{M}_j] + k_{-x}[\mathrm{HD}] + k'_{-x}[\mathrm{HD}]} \tag{19}$$

In the case of the $H_2 + D_2$ reaction, at low extents of conversion, the terms containing [HD] in eq 17 and 18 may be neglected. Then $M_{1,2,3}$ represent Ar, H_2, and D_2 and eq 20 applies. When HD is the only initial reactant, at the limit of low conversions, one may neglect in eq 19 all terms which have $[H_2]$ and $[D_2]$ as factors and obtain

$$\frac{\mathrm{d}[\mathrm{HD}]}{\mathrm{d}t} \rightarrow 2k'_x[\mathrm{H_2}][\mathrm{D_2}^{(\mathrm{v})}]_{\mathrm{ss}} + 2k_x[\mathrm{D_2}][\mathrm{H_2}^{(\mathrm{v})}]_{\mathrm{ss}} \approx$$

$$2k'_{\epsilon1}[\mathrm{D_2}][\mathrm{Ar}]\left\{\frac{1 + \dfrac{k'_{\epsilon2}[\mathrm{H_2}]}{k'_{\epsilon1}[\mathrm{Ar}]} + \dfrac{k'_{\epsilon3}[\mathrm{D_2}]}{k'_{\epsilon1}[\mathrm{Ar}]}}{1 + \dfrac{k'_{-\epsilon1}}{k'_x}\left[\dfrac{[\mathrm{Ar}]}{[\mathrm{H_2}]} + \dfrac{k'_{\epsilon2}}{k'_{\epsilon1}} + \dfrac{k'_{\epsilon3}[\mathrm{D_2}]}{k'_{\epsilon1}[\mathrm{H_2}]}\right]}\right\} +$$

$$2k_{\epsilon1}[\mathrm{H_2}][\mathrm{Ar}]\left\{\frac{1 + \dfrac{k_{\epsilon2}[\mathrm{H_2}]}{k_{\epsilon1}[\mathrm{Ar}]} + \dfrac{k_{\epsilon3}[\mathrm{D_2}]}{k_{\epsilon1}[\mathrm{Ar}]}}{1 + \dfrac{k_{-\epsilon1}}{k_x}\left[\dfrac{[\mathrm{Ar}]}{[\mathrm{D_2}]} + \dfrac{k_{\epsilon2}[\mathrm{H_2}]}{k_{\epsilon1}[\mathrm{D_2}]} + \dfrac{k_{\epsilon3}}{k_{\epsilon1}}\right]}\right\} \tag{20}$$

$$[\mathrm{HD}^{(\mathrm{v})}]_{\mathrm{ss}} = \frac{\sum\limits_j \varkappa_{\epsilon j}[\mathrm{M}_j][\mathrm{HD}]}{\sum\limits_j \varkappa_{-\epsilon j}[\mathrm{M}_j] + (k_{-x} + k'_{-x})[\mathrm{HD}]} \tag{21}$$

Here M_1 and M_2 correspond to Ar and HD, respectively. Equation 21 is identical with eq 9 except that $\varkappa_x$ has been replaced by $(k_{-x} + k'_{-x})$. This leads to a corresponding redefinition for α

$$\alpha \equiv (k_{-x} + k'_{-x})/\varkappa_{-\epsilon1}$$

and the rate of exchange is given by eq 10. A correspondence between the two extremes of disequilibrium follows from the above. Since $K_{\mathrm{eq}} = 4$ for the exchange step at these temperatures

$$\frac{\varkappa_{-\epsilon1}}{k'_{-x}}\frac{k'_x}{k'_{-\epsilon1}} = 4\frac{\varkappa_{-\epsilon1}}{k'_{-\epsilon1}} \approx 4\frac{\varkappa_{\epsilon1}}{k'_{\epsilon1}} \tag{22}$$

The excitation rate constants $\varkappa_{\epsilon1}$ and $k'_{\epsilon1}$ and the ratios on the left side of eq 22 have been obtained experimentally; hence this equation imposes a quantitative condition which relates two independent sets of measurements. The results are summarized in Table IV.

Table IV. Compatibility of Kinetic Parameters for $(H_2 + D_2)$ *vs.* 2HD[a]

α	γ	$10^{-3}\varkappa_{\epsilon1}$, l. mole^{-1} sec^{-1}	$\alpha^{-1}k'_x/k'_{-\epsilon1}$	$\varkappa_{\epsilon1}/k'_{\epsilon1}$
1000	25	1.51	0.15	0.67
250	15	2.14	0.60	0.94
125	7	2.88	1.20	1.27
100	5	3.26	1.50	1.43
80	3	3.72	1.88	1.63

[a] Combinations of α and γ cover the acceptable range deduced from the HD investigation. Values of $k'_{\epsilon1}$ and $k'_x/k'_{-\epsilon1}$ are given in the text.

For the $H_2 + D_2$ exchange, Bauer and Ossa reported $k'_{\epsilon1} = 9.1 \times 10^3$ (l. mole^{-1} sec^{-1}) at 1400°K, and $k'_x/k'_{-\epsilon1} \approx 150\ (\pm 25)$. Also $k_x/k'_x = k_{-x}/k'_{-x} \approx 0.3$. Thus, the ratio $k'_{-x}/\varkappa_{-\epsilon1}$ in eq 22 is a close approximation to the parameter α which was determined in this study of HD self-exchange.[11] For the range of acceptable α's and γ's, the corresponding $\varkappa_{\epsilon1}$ values have been calculated and listed ($\varkappa_{\epsilon1}$ varies inversely with α and γ) in Table IV; eq 22 is satisfied for $\alpha = 100$–125 and $\gamma = 5$–7, and these are in the acceptable kinetic range.[6,7] This result, while gratifying at first view, is in some measure accidental. It is not uncommon for two sets of shock-tube data for the same reaction taken a few weeks apart on the same apparatus to differ by as much as a factor of 2. The $H_2 + D_2$ data were taken about 4 years ago and the shock tube and method of operation have been changed somewhat since then. Furthermore, the two-state excitation model upon which this comparison is based is an oversimplification which adds uncertainty to the quantitative parameters. Hence any ratio $\varkappa_{\epsilon1}/k'_{\epsilon1}$ which falls within a factor of 4 of that expected from eq 22 should be considered acceptable. Still, the combination with $\alpha = 1000$ ($\gamma = 25$) which causes eq 22 to fail by more than a factor of 4 requires a value of γ which is much higher than that suggested by the independent vibrational relaxation data.[6,7]

Another comparison to be made concerns the empirically deduced activation energies. For the $H_2 + D_2$ exchange, Bauer and Ossa reported 42.7 kcal/mole for $k_{\epsilon1(\mathrm{D_2} \leftarrow \mathrm{Ar})}$. Burcat and Lifshitz did not calculate excitation rate constants; their data reduced on the same basis would probably give a value close to 39 kcal/mole. These values are significantly higher than the value of 34.5 kcal/mole reported here for $\varkappa_{\epsilon1(\mathrm{HD} \leftarrow \mathrm{Ar})'}$, considering that the estimated limits of error of these values are ±2 kcal/mole. The following is a rationalization of this discrepancy. On the basis of the proposed mechanism, the experimental activation energy is the sum of θ, the effective energy of activation for exciting the reactive species out of its ground state, and $(E_v - E_0)$, the energy above the ground state of the lowest level v from which exchange readily occurs. Bauer and Ossa plotted values for $RT/p\tau_v$[6] *vs.* $1/T$ to obtain an equivalent Arrhenius expression: $\eta_{10} = \eta_{10}^0 \exp(-\beta\theta)$. For $D_2 \leftarrow Ar$ at 1400°K they found $\eta_{10} = 10^{11.5} \exp(-13{,}350/RT)$, mole^{-1} cm^3 sec^{-1}. This led to $E_v = 29.3$ kcal/mole for $k_{\epsilon1}(\mathrm{D_2} \leftarrow \mathrm{Ar})$, which corresponds closely to $v = 4$ for D_2 (and $v = 3$ for H_2). No vibration relaxation measurements have been reported for HD, and θ may be different owing to either the wider spacing of its vibrational levels or the asymmetry of the HD molecule. If we carry over $\theta = 13.35$ kcal/mole to $HD \leftarrow Ar$, then the corresponding $E_v = 21.15$ kcal/mole for $\varkappa_{\epsilon1}(\mathrm{HD} \leftarrow \mathrm{Ar})$, which is somewhat below $v = 3$ for HD. A change in θ of only 2 kcal/mole plus the experimental uncertainty could account for this difference. However, it is also likely that the probability for exchange does not increase abruptly at a particular level; rather, that it rises rapidly over a series of levels in some

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(11) In the above approximation for α, neglect of k_{-x} removes the necessity of including the term $(k_x/k_{\epsilon-1})$ in deducing an expression such as eq 22. Since the relative uncertainty in the evaluation of $k_x/k_{-\epsilon1}$ was somewhat greater than for $k'_x/k'_{-\epsilon1}$ (corresponding inversely to thus relative importance of $H_2^{(\mathrm{v})}$ and $D_2^{(\mathrm{v})}$ terms in the rate expression), we feel that inclusion of $k_x/k_{-\epsilon1}$ would result in a less accurate criterion for comparison than eq 22. The results in Table IV would not be altered significantly.

manner which may depend upon the translational or rotational energies of the colliders. The critical level, as identified from the deduced activation energy for $\kappa_{\epsilon 1}$, represents a weighted average.

The consistency of the two sets of data is encouraging. The fact that different gases were used in the two studies, and that improvements were made during the past 4 years in methods of preparing and handling uncontaminated samples in our laboratory make it unlikely that this degree of consistency could have been achieved if the observed products were produced by reactions induced by contaminants. The observed vastly increased rates for HD exchange in samples known to contain oxygen and the report by Dr. A. Lifshitz that a different power rate expression was found for samples which had 0.01% O_2 present help to substantiate this conclusion. However, it is evident that the role of oxygen in initiating a chain mechanism is not known in detail. The transition region from a few parts per million to 10^3 ppm of O_2 merits careful investigation.

Acknowledgments. We wish to thank Dr. Assa Lifshitz and Mr. Alexander Burcat, of the Hebrew University of Jerusalem, for providing us with their HD exchange data prior to publication. Thanks are also due Dr. Lifshitz and Mr. Harvey Carroll for invaluable assistance with the HD purification. Dr. Nicholas Zevos conducted the series of experiments using unpurified HD which were run at this laboratory. Acknowledgment is made of a supporting grant from the Petroleum Research Fund, administered by the American Chemical Society.

Appendix. On Removing Oxygen from Hydrogen Deuteride without Scrambling[12]

A sample of HD (1% air; 0.21% D_2) was adsorbed at liquid nitrogen temperatures onto Pittsburgh activated charcoal, Type BPL. The adsorbent had been thoroughly pumped on while being heated to 400° for 30 min. The adsorbent–adsorbate system was kept at liquid nitrogen temperatures for about 10 hr and then allowed to warm up to room temperature. Essentially all the HD came off rapidly; it contained no N_2 or O_2 (<0.002%). There was no discernible increase in D_2.

The following is a partial listing of various tests made during the course of developing the above simple procedure. All samples of HD were approximately 50 cm l. at room temperature and were adsorbed onto 20 g of the activated charcoal.

(a) When the sample of HD was maintained on the adsorbent at liquid nitrogen temperatures for only 30 min and then raised to the temperature of Dry Ice, the desorbed gas was identical in composition with that of the original material.

(b) When a sample was adsorbed at liquid nitrogen temperatures for a few minutes and then slowly warmed up so that only small quantities of gas were desorbed at a time, the oxygen and nitrogen contaminants were reduced to about half their original magnitudes. Again there was no self-exchange of the HD. Hence, maintaining the gas in the adsorbed state at liquid nitrogen temperatures for about 10 hr appears to be necessary for binding the oxygen and nitrogen contaminants sufficiently tightly to permit the prior evolution of the HD when the sample is heated to room temperature.

(c) A sample of HD was adsorbed onto activated charcoal at liquid nitrogen temperatures and maintained for 2 hr. The equilibrium gas ($\approx$3 mm) was toeplered to another container. That gas showed no detectable oxygen or nitrogen (<0.001%). This is an alternate procedure, but a bothersome one, as is a procedure based on a vpc column maintained at low temperatures.

(d) Pure HD was allowed to contact degassed activated carbon at room temperature for 72 hr. Although there was no apparent adsorption as measured by a decrease in pressure, the sample was found to contain 6.3% D_2. Clearly, self-exchange occurs on the surface even though the equilibrium amount adsorbed at room temperature is very small. Spectrographic analysis of the activated carbon has shown the presence of considerable amounts of iron, magnesium, and aluminum.[13]

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(12) Performed with the active collaboration of Assa Lifshitz and Harvey Carroll.

(13) Thanks are due to Dr. R. Skogerboe for performing this analysis.