Magnetic Deshielding of Protons Due to Intramolecular Steric Interactions with Proximate Hydrogens

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Abstract: Hydrogen atoms which are subject to significant steric compression generally exhibit a chemical shift to lower field. The degree of deshielding experienced by a perturbed hydrogen, H, is dependent upon the geometrical relationship existing between the H–C bond and the interacting hydrogen, H′. An expression is obtained relating the magnitude of the steric shift to the component of the H′H repulsive force directed along the H–C axis. A comparison is drawn between the proton and C^{13} steric shifts which result from the H′H interaction. The two effects are explained in terms of sterically induced charge polarization in the H–C^{13} bond.

The recent literature contains several articles describing proton deshielding due to intramolecular steric interactions with other proximate hydrogen atoms.[1–8] Although many conjectures have been made concerning the nature of the deshielding mechanism, no satisfactory quantitative expression for the effect has been devised as yet. Since steric shifts appear to have an intricate dependence upon the structure and geometry of a molecule, it is highly desirable to obtain an equation expressing the relationship. Such an expression would not only prove useful in determining the physical basis for the shifts, but would also aid in relating observed nmr spectral data to specific structural factors in a molecule.

In the present paper, the steric shift, δ_s^H, is correlated with the component of the nonbonded hydrogen–hydrogen repulsive force along the H–C bond axis. The model proposed to explain the deshielding involves induced electronic charge polarization in the H–C bond as a result of the H′H interaction. As the chemical shifts exhibited by the C^{13} nuclei bonded to such overcrowded hydrogens have been successfully explained[9–12] using these concepts, it is felt that the proton steric shifts should be amenable to a similar approach.

Results and Discussion

A. Proton and Carbon-13 Steric Shifts. It has been demonstrated that nonbonded repulsions between proximate hydrogens in a molecule often cause an increase in the shielding experienced by the associated C^{13} nuclei.[9–12] Grant and Cheney[9] found a linear relationship between the magnitude of the C^{13} chemical shift and the force component along the H–C^{13} bond axis. The empirical chemical shift expression may be expressed as

$$\delta_s^{C^{13}} = 1680 \sum_i \cos\theta_i \exp(-2.671 r_i) \qquad (1)$$

where $\delta_s^{C^{13}}$ is the steric shift of the carbon-13 nucleus measured in parts per million, r_i is the distance between the interacting pair of hydrogens, and θ_i is the angle between the extension of the H_i–H internuclear line and the H–C^{13} bond of interest as shown in Figure 1. Summation is taken over all hydrogens, H_i, which significantly interact with the atom, H, in the bond under consideration. The effect was rationalized in terms of induced charge polarization in the bond as a result of the nonbonded hydrogen–hydrogen repulsive forces.

It is now proposed to extend the correlation to obtain an expression for proton chemical shifts caused by similar steric interactions. If the model involving slight charge polarization in the perturbed bond is correct, both $\delta_s^{C^{13}}$ and δ_s^H should be linearly related to the factor

$$f(r_i,\theta_i) = \sum_i \cos\theta_i \exp(-2.671 r_i) \qquad (2)$$

which expresses the geometric functionality of the force components along the H–C bond axis. A simple calculation is undertaken in the following paragraph to justify this expectation and to indicate the general form of the relationship.

Assuming a change in electronic charge density of amount $\Delta\rho_H$ on the hydrogen, H, as a result of the steric interactions, the variation in magnetic shielding may be given by the Lamb formula[13]

$$\delta_s^H = 10^6 e^2 \Delta\rho_H / 3mc^2 a_0 = 17.8\Delta\rho_H \qquad (3)$$

The assumption of charge transfer in the H–C^{13} bond yields eq 4, where the second approximation employs

$$\Delta\rho_H \approx -\Delta\rho_{C^{13}} \approx -\delta_s^{C^{13}}/200 \qquad (4)$$

Lauterbur's[14] empirical relationship for carbon-13 chemical shifts in terms of variations in charge density on the carbon atom. Substitution of (4) and (1) into (3) gives

$$\delta_s^H \approx -150 \sum_i \cos\theta_i \exp(-2.671 r_i) \qquad (5)$$

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Table I. Structural Parameters and Proton Steric Shifts for Systems Given in Figure 2

Structure	H_i[a]	r_i, Å	Cos θ_i	Exp($-2.671r_i$) × 10^2	f(r_i,θ_i) × 10^2	δ_s^H,[b] ppm
I	H′	1.720	0.5000	1.0113	0.5056	−0.55 ± 0.077
II	H′	1.720	0.5000	1.0113	1.0113	−1.14
	H″	1.720	0.5000	1.0113		
III	H′	1.806	0.3640	0.8045	0.2928	−0.34
IV	H′	1.937	0.4676	0.5665	0.2648	−0.195 ± 0.015
V	H′	2.513	0.0564	0.1217	0.0068	0.0
VIa[c]	H′	1.874	0.4962	0.6708	0.1919	−0.095 ± 0.022
	H″	2.054	−0.3404	0.4142		
VIb[d]	H′	1.996	0.4460	0.4841	0.1322	
	H″	2.152	−0.2506	0.3342		

[a] Designation of proton interacting with H to produce the steric shift, δ_s^H. [b] The average and standard deviations are listed for those interactions where more than one case was treated. Cobb and Memory[8] report 19 measurements for structures of type I. Nagata and coworkers[5] give 15 observations of type IV and two each of types V and VI. [c] Structure VIa resulted from a least-squares adjustment of atomic coordinates in VI using standard bond angles and distances as conditions. [d] The data for VIb were determined in the same way as those of VIa, except that a 2.0-Å separation between H and H′ was imposed as an additional constraint.

For the case of phenanthrene (structure I in Figure 2), where $\theta_i \approx 60°$ and $r_i \approx 1.72$ Å, eq 5 yields $\delta_s^H \approx -0.76$ ppm. This compares reasonably well in magnitude with the observed value of −0.54 ppm given by Cobb and Memory[8] for the van der Waals deshielding in phenanthrenic systems. As with eq 1, the expression cannot be expected to give satisfactory results in situations where r_i is less than 1.7 Å. This constraint is due to the breakdown at closer distances of the simple exponential law used to express the nonbonded hydrogen–hydrogen interactions.[9] There should also be an additional limitation in the use of eq 5 when f(r_i,θ_i) is negative since the net repulsive force on H would tend to polarize its charge cloud in a direction away from the associated carbon atom. Although the resultant distortion of the hydrogen orbital in such a case should also produce shielding variations at the proton, this second-order effect generally would be small compared to the shifts under discussion at present.

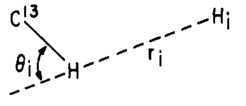

Figure 1. The geometric parameters, r_i and θ_i, are used in calculating steric shifts of the nuclei in the H–C^{13} bond which result from the H_iH interaction.

B. Empirical Correlation of Proton Steric Shifts. In order to confirm the linear dependence of δ_s^H on f(r_i,θ_i) and obtain an expression which will yield better quantitative results than eq 5, an empirical correlation is considered using data from compounds containing the basic structures portrayed in Figure 2. The geometric parameters and observed steric shifts for the six structures are listed in Table I. It should be noted that structures I and IV–VI contain only those portions of the compounds actually employed which are necessary to indicate the nature of the different steric interactions. Each of the shifts given for these structures represents an average of two or more cases involving various molecules. The information presented in Table I is discussed further in succeeding paragraphs.

Memory and coworkers[8,15] have successfully related the proton shifts in a number of polycyclic hydrocarbons to ring-current effects calculated using McWeeny theory.[16] In their study, the local shielding contributions were subtracted from the experimental results by referencing all chemical shifts to benzene and then adding an empirical shift of 1.55 ppm to account for the benzene ring current. The only major discrepancies in the resulting correlation involved excessive deshielding of protons subject to large steric interactions such as those in structures I–III. It was noted that the shifts of protons having the phenanthrenic geometry (I) could be brought into line by subtracting a steric contribution of approximately 0.54 ppm. They also reported van der Waals shifts for 1,2,7,8-dibenzanthracene (II) and 3,4-benzophenanthrene (III) which are significantly different from the phenanthrenic value.

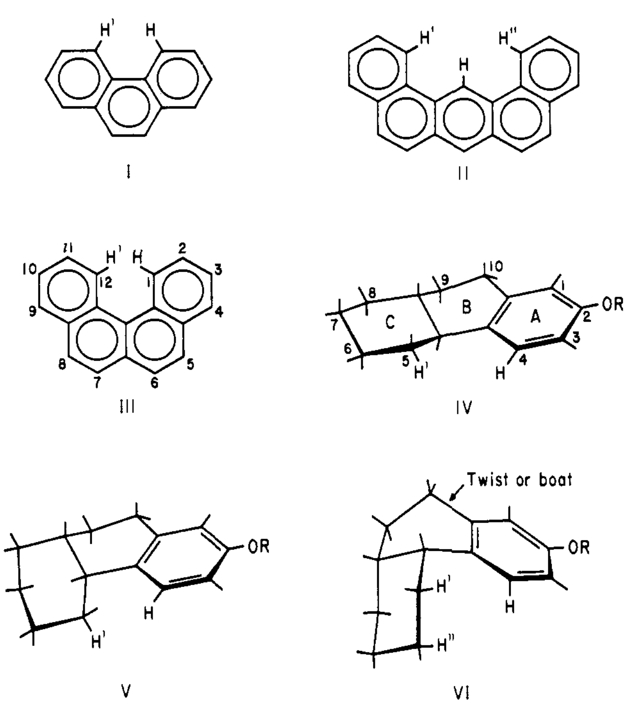

Figure 2. Various structures are given which contain protons, H, exhibiting steric shifts due to van der Waals interactions with proximate hydrogens indicated by H′ and H″. In IV–VI, R is either H or CH_3.

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Table II. Atom Coordinates for Structures VIa and VIb Obtained by a Least-Squares Procedure Using Standard Bond Lengths and Angles as Constraints[a]

Atom	VIa X	VIa Y	VIa Z	VIb X	VIb Y	VIb Z
C_1	1.1495	−2.0093	0.4033	1.1555	−2.0028	0.4226
C_2	−0.0544	−2.7113	0.2630	−0.0432	−2.7140	0.2799
C_3	−1.2544	−2.0050	0.1010	−1.2488	−2.0156	0.1285
C_4	−1.2257	−0.6205	−0.1057	−1.2300	−0.6311	−0.0849
C_{4a}	−0.0012	0.0582	−0.1340	−0.0113	0.0559	−0.1166
C_{4b}	0.0111	1.5831	−0.0039	0.0049	1.5815	0.0004
C_5	−1.3531	2.0455	0.5435	−1.3471	2.0632	0.5588
C_6	−1.6352	1.3343	1.8801	−1.6343	1.3392	1.8867
C_7	−0.5301	1.6846	2.8935	−0.5215	1.6641	2.9005
C_8	0.8362	1.2331	2.3444	0.8420	1.2182	2.3406
C_{8a}	1.1137	1.9502	1.0104	1.1146	1.9463	1.0111
C_9	2.4853	1.5349	0.4656	2.4834	1.5358	0.4566
C_{10}	2.5164	0.0732	0.0140	2.5111	0.0787	−0.0112
C_{10a}	1.1780	−0.6214	0.2144	1.1774	−0.6187	0.2086
H	−2.1489	−0.0759	−0.2476	−2.1471	−0.1223	−0.3502
H′	−2.1431	1.7966	−0.1805	−2.1485	1.8648	−0.1641
H′′	−1.6589	0.2461	1.7211	−1.6716	0.2534	1.7150

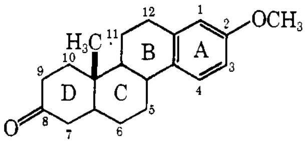
[a] A separation of 2.0 Å between H and H′ was given as an additional condition for structure VIb.

Nagata, Terasawa, and Tori[5] determined the steric shifts of the aromatic C_4 proton due to interaction with an equatorial C_5 hydrogen in a number of compounds having structural similarities to various possible conformations of A-ring aromatic octahydrophenanthrene (IV–VI in Figure 2). Shielding effects other than the van der Waals interaction were effectively cancelled by using the aromatic C_1-hydrogen as internal reference in all molecules studied and then comparing the resultant shift of the C_4 proton with the value obtained for 2-methoxy-5,6,7,8-tetrahydronaphthalene in which no significant overcrowding is possible. It was shown that bond anisotropies in the C ring have a negligible effect on the C_4-proton shift. Hence, the observed net deshielding could arise only through steric interactions. The authors pointed out a strong relationship between the degree of deshielding and the distance separating the C_4 and C_5 protons in the different structures.

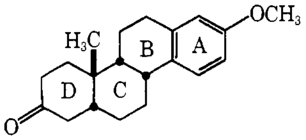
The values of r_i and θ_i in Table I were calculated for structures other than III and VI by employing normal bond angles of 109° 29′ and 120° for tetrahedral and trigonal carbon atoms, respectively. In the aromatic rings, H–C bond lengths were taken as 1.08 Å, and the separation between carbons was assumed to be 1.40 Å. The carbon–hydrogen distance used in the saturated portions of structures IV and V was 1.10 Å, while the carbon–carbon bonds were assigned values of 1.54 Å. Bonds involving an aromatic ring carbon and a saturated carbon were taken as 1.52 Å. Although minor deviation from these standard geometric parameters is expected in the actual molecules, the given quantities are considered to be valid as a working hypothesis.

Owing to severe steric interactions in 3,4-benzophenanthrene, the molecule is seriously distorted out of the plane. Since the normal bond distances and angles would lead to erroneous results in this case, the geometry of the molecule was determined from a least-squares refinement[17] of the X-ray crystallographic data given by Herbstein and Schmidt.[18] The coordinates of the C_1-hydrogen, H, were calculated by assuming that C_1 and the atoms to which it is bonded form a plane. In this computation, the H–C_1 separation was taken as 1.08 Å and the distances from H to the carbon atoms adjoining C_1 were chosen to be equal. The resulting bond angles differ only slightly from the usual 120° value accepted for aromatic carbons. Similar assumptions were employed in determining the position of the hydrogen, H′, at C_{12}.

In ref 5, two molecules (VII and VIII) were reported to possess conformational similarities to structure VI. A twist or boat conformation is forced upon the B ring in both of these compounds as a result of steric repulsions involving the C_{12}-methylene group. The methyl and C_{10}-methylene groups are the interacting species in VII and VIII, respectively. In the absence of experimentally determined bond distances and angles for these compounds, it is necessary to calculate the structural parameters using assumed values for the quantities. However, uncertainties in the degree of strain experienced by the B ring makes such a course of action extremely difficult. As a result, the geometrical relationships for structure VI cannot be expressed with the same degree of confidence as the relationships in structures I–V. Although this precludes the use of VI in a determination of the best straight-line fit of the data, two approximate calculations of the molecular geometry were made in order to gain some insight into the nature of the steric shifts experienced by the aromatic C_4 proton in the compounds with a skewed B ring.



VII



VIII

The atomic coordinates used for the type-VI structures were obtained by the Waser[19] least-squares procedure which employs various interatomic distances as conditions in fitting the molecular geometry. Normal bond lengths and angles were imposed as constraints by specifying the appropriate separations for all 1,2 and

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(17) D. J. Duchamp, private communication. Variation of the atomic coordinates and isotropic temperature factors was continued until an *R* value of 0.168 was achieved.

(18) F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 3302 (1954).

(19) J. Waser, *Acta Crystallogr.*, **16**, 1091 (1963).

1,3 atom pairs in the calculation. In addition, all 1,4 distances were given in the A and C rings to maintain the respective planar and chair conformations. It might be expected that the deformation accompanying a strained twist or boat form of the B ring would generally affect bond lengths to a lesser extent than bond angles. Hence, distances between adjacent atoms were assigned a heavier weight than the separations of nonbonded atoms in the least-squares analysis. The atomic coordinates resulting from this calculation are listed under structure VIa in Table II. As may be determined from the atom positions, deviations from the standard bond lengths and angles are generally insignificant. The only major variations occur in the B ring where some angles differ by as much as 3° from the normal values.

In calculating the atomic coordinates given for VIb in Table II, an arbitrary separation of 2.0 Å between H and H′ was given as an additional constraint with all other conditions remaining unchanged. Although this H′H distance is 0.13 Å greater than that in VIa, the increased separation was accommodated easily by minor adjustments in bond lengths and angles throughout the structure. The over-all geometry of VIb is therefore very similar to the conformation of VIa.

Figure 3 contains a plot of δ_s^H *vs.* $f(r_i,\theta_i)$ which shows, within the limits of errors inherent in the treatment, a linear relationship having the form

$$\delta_s^H = -105\sum_i \cos\theta_i \exp(-2.671r_i) \qquad (6)$$

Since the intercept of the least-squares line through the data points for structures I–V falls at 0.0117 ppm, it has been neglected in eq 6. The slight scatter in the points can be attributed for the most part to minor deviations in the structural parameters used to calculate r_i and θ_i. However, there is also some uncertainty in the δ_s^H values for structures I–III as a result of inaccuracies in the ring current contributions to the chemical shifts which were of necessity computed theoretically.[15] As there is no reason to believe that serious error should result from these considerations, the correlation is felt to be quite satisfactory. Agreement in form and order of magnitude between the empirical relationship for proton steric shifts and the predicted expression given by eq 5 lends additional weight to the proposal that charge transfer is induced in sterically perturbed bonds.

The data points for VIa and VIb indicate that the structures may represent fairly close approximations to the actual molecular conformations in systems containing the structural elements of VI. Regardless of the exact geometrical relationships, a B ring in the twist or boat form forces both H′ and H′′ to maintain rather close steric contact with H. If the steric effect were dependent only upon the separation of the interacting hydrogen atoms (*i.e.*, the total van der Waals compression[5]), a much greater shift would be expected than the observed 0.095 ppm. Since an estimate of the relative compression experienced by the hydrogens of interest in structures I–VIb may be obtained by comparing the exponential terms in Table I, it is possible to demonstrate the basis for this supposition. The totals of the H′ and H′′ terms in VIa and VIb are quite similar to the respective exponential values for I and III so that deshielding in the range of 0.3 to 0.6 ppm might be expected for type-VI compounds if the over-all nonbonded repulsive force were the determining factor in steric shifts. As much better agreement with the experimental shift is realized by correlation with $f(r_i,\theta_i)$ than with $\exp(-2.671r_i)$, support is given to eq 6 and the hypothesis that the *net force component* along the H–C bond axis induces the van der Waals shifts.

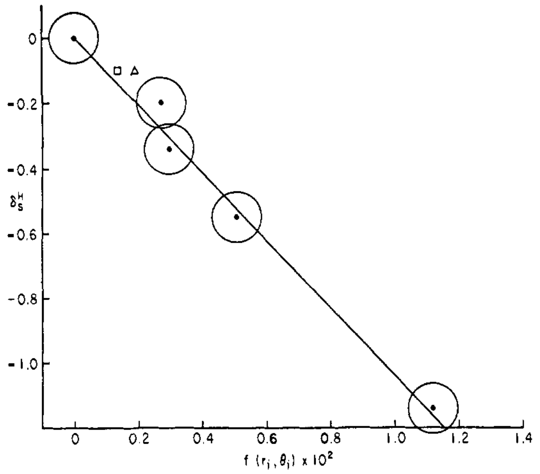

Figure 3. The observed steric shifts of H in structures I–VI are plotted against $f(r_i,\theta_i)$ which is defined by eq 2. No estimate of error is possible for the approximate type-VI structures which are represented by △ (VIa) and □ (VIb).

C. Comparison of Steric and Electric Field Effects. Since a group in the molecule which possesses a net charge can polarize the H–C bond in a manner similar to that postulated as a basis for the steric shifts, a comparison of the chemical shift expressions describing the two effects appears to be merited. It has been noted that the electric field at a particular proton arising from polar groups in other parts of a molecule can lead to a chemical shift which is dependent upon both the first and second powers of the field strength.[20] The relationship for the shift in ppm may be given approximately as

$$\delta_E^H \approx -2 \times 10^{-6}E_z - 10^{-12}E^2 \qquad (7)$$

where E_z is the component of the field strength along the H–C bond. Musher[21] showed that the term proportional to E_z results from polarization of the bonding electrons. Marshall and Pople[22] demonstrated that distortion of the hydrogen orbital by the electric field produces the shielding variations which are proportional to E^2. If the intramolecular fields are randomly oriented, the linear term in eq 7 is averaged to zero, and the quadratic term, although small, predominates. However, the presence of a polar group in the molecule can result in a net field with magnitude of the order 10^5 esu. In such a case, the shielding due to bond polarization (~0.2 ppm) is ~20 times greater than the shift produced by orbital distortion.

Fluctuating dipole fields resulting from dispersion forces have been proposed in the past as a possible cause of steric shifts.[4,8] However, such effects are

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[20] A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).
[21] J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).
[22] T. W. Marshall and J. A. Pople, *Mol. Phys*, **1**, 199 (1958).

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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(5) A. Bar-Nun and A. Lifshitz, *ibid.*, **47**, 2878 (1967).