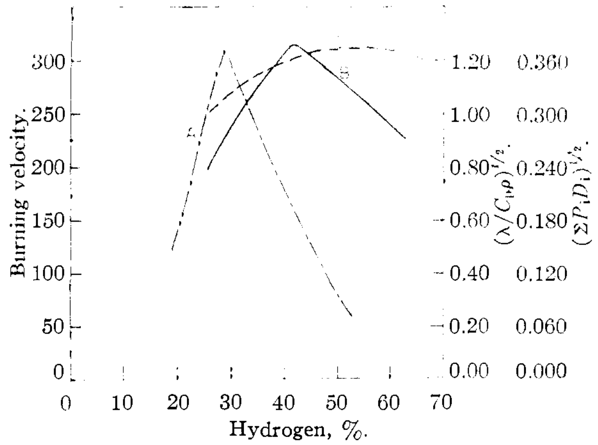

Fig. 2.—A plot of mixture strength (volume % hydrogen) *vs.* A, $[\Sigma(P_iD_i)]^{1/2}$; B, burning velocities, cm./sec.; C, $(\lambda/C_p\rho)^{1/2}$.

seems to be well established. Nevertheless, as Tanford[14] has shown, there is a general correlation over a broad range of compositions in which molecular hydrogen concentration is kept constant, but the flame temperature is varied by varying the O_2/N_2 ratio. It is only when the molecular hydrogen concentration is varied that the discrepancy becomes serious.

The applicability of a thermal theory is now to be considered. In general, most thermal theories deal with a "thermal" parameter such that[15]

$$S^2 \propto \left[\frac{\lambda}{C_p\rho}\right] \qquad (2)$$

where λ is the thermal conductivity, C_p is the average molecular heat capacity, and ρ is the gas density, all calculated for the initial mixture at the flame temperature. The term in equation 2 is given for each mixture in the last column of Table I.

The variation of $[\lambda/C_p\rho]^{1/2}$ with the mixture strength is shown in Fig. 2, curve C. It is obvious that the thermal parameter produces an almost equal but opposite deviation from that of the Tanford diffusion theory, maximizing at substantially higher hydrogen concentrations (~55%).

It appears from this work, therefore, that neither a simple diffusion theory nor a thermal theory applied exclusively can adequately explain the experimental data in this example. It should be possible to set up an empirical relation involving both 1 and 2 that would yield a closer correspondence to observation, but this point was not pursued further. Such a relation would be based on the presumption that the greater conductivity of hydrogen-rich mixtures results in a higher average flame temperature.

It may also be pointed out that neither approximation takes any account of the peculiarities of the reaction kinetics as deduced from observations on the slow (low temperature) reaction.[16] In particular, it will be recalled that there is strong evidence for chain branching, for which no allowance has been made in the above. It is also true that low-temperature rates are substantially greater at high hydrogen concentrations, a result in qualitative agreement with the burning velocity data. In terms such as these, a closer understanding of hydrogen–air flames will doubtless be achieved.

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[15] M. Evans, *Chem. Revs.*, **51**, 363 403 (1952); A. G. Gaydon and H. G. Wolfhard, "Flames," Chapman and Hall, Ltd., 1953, p. 117.

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[Contribution from the Department of Chemistry of The Pennsylvania State University]

A Simple Model for Barriers to Internal Rotation

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A number of symmetrical barriers to internal rotation about single bonds in molecules have been calculated on the assumption that the barriers were caused by ordinary van der Waals repulsions between non-bonded atoms or groups of atoms in the molecules. The repulsions have been estimated by analogy with known repulsions between similar atoms or groups of atoms which are not part of a larger molecule, with allowances made for any residual electrical charges on the atoms or groups. The calculations based on this simplified model indicate that in most cases about half the barrier can be attributed to van der Waals repulsion forces. It is suggested that the remainder can perhaps be explained on the basis of the electrostatic interactions between the charge distributions of the chemical bonds, as originally suggested by Lassettre and Dean (ref. 9) and by Oosterhoff (ref. 3). Although it is admittedly rather empirical, the model seems capable of furnishing reasonable estimates of steric repulsions.

The interactions between non-bonded atoms in molecules seem to be responsible for a large number of phenomena in chemistry and physics. These interactions influence the spectra and thermodynamic properties of many substances, are responsible at least in part for the existence of certain rotational isomers, and cause certain configurations of complex molecules to be preferred over others.[2,3] Furthermore, if these interactions change on going from a reactant to a product (or a transition state), the equilibrium constant (or rate constant) for the reaction is affected. Such effects on reactivity are

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[1] Institute of Molecular Physics, University of Maryland, College Park, Maryland.

[2] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, Inc., New York, N. Y., 1954.

[3] L. J. Oosterhoff, Thesis, Leiden, 1949; *Disc. Faraday Soc.*, **10**, 79, 87 (1951).

usually termed "steric effects." In some reaction series, these steric effects are so important as to largely determine relative rates or positions of equilibrium.[4,5] The energies involved are usually of the order of magnitude of a few kcal. per mole. The origin of these interactions has been uncertain[6,7] and it seems likely that several effects may each contribute appreciably to the interaction energy.

Among the simplest phenomena caused by interactions between non-bonded atoms in molecules are the barriers to internal rotation about single bonds. Since these barriers have been known to exist for some time and a considerable body of experimental evidence pertaining to their size has been accumulated, they provide a convenient body of data on which to test proposed methods of calculating such interactions.

In principle a complete quantum mechanical treatment of a molecule would yield the barrier to internal rotation along with all the other properties of the molecule. In practice drastic approximations are necessary, and it is therefore not too surprising that quantum mechanical methods have met with little success in the calculation of such a small energy difference. Thus application of first-order perturbation procedure to the usual valence bond structure,[8a] and resonance with double bonded structures,[8b] have not yielded results in accord with experiment in the case of ethane.

There have been a number of more empirical attempts to explain the origin of barriers to internal rotation, none of which appears to have been entirely successful. The most promising attempt seems to be that of Lassettre and Dean,[9] who considered that the barriers originate in the electrostatic interactions between the dipole and quadrupole moments of the *bonds*. Since the quadrupole moments were not known, experimentally determined barriers were used to calculate the bond quadrupole moments. The calculated moments were not unreasonable, but recent evidence from microwave pressure broadening indicates that the real quadrupole moments may be considerably smaller.[10] This is serious, since the calculated barriers are very sensitive to the value of the bond quadrupole moment. Oosterhoff[3] has carried out a thorough theoretical discussion from much the same point of view and finds that the effect of higher multipoles may be of importance. More empirical approaches have been made by Aston, Isserow, Szasz and Kennedy,[11] and by French and Rasmussen,[12] who adopted the idea of simple van der Waals repulsion between atoms, but had to use values of known barriers to determine the repulsions, rather than calculate barriers from known repulsions.

In the present paper, these barriers to internal rotation have been compared with calculations based on the assumption that the barriers are caused by ordinary van der Waals repulsions between non-bonded atoms or groups of atoms in the molecules. The repulsions have been assumed to be the same as those between similar fragments existing as free particles. For example, the force law governing the interactions between two fluorine atoms bonded to different parts of a larger molecule have been assumed to be the same as the force law governing the interactions between two isolated neon atoms, allowance being made for any residual electrical charge on the fluorine atoms. Since the force laws which are used arise from well-founded calculations or experimental results, no approximate quantum mechanical methods need be used. The major approximation involved, aside from the conceptual model itself, is the assignment of the force laws, which is discussed below. For the sake of simplicity, only barriers which are symmetrical and not complicated by rotational isomerism have been considered. As will be seen, the calculations indicate that in most cases about half of the barrier can be attributed to van der Waals repulsion forces and that the remainder can perhaps be explained on the basis of the model used by Lassettre and Dean[9] and by Oosterhoff.[3]

The simple model that has been employed, assuming ordinary van der Waals repulsions between non-bonded atoms or groups, is not new. In addition to those already mentioned,[11,12] a number of workers have used this model to explain the vibrations of many simple molecules,[13–15] and to discuss the dipole moments of non-rigid molecules.[16] The model has also been employed in the calculation of steric effects by Westheimer and Mayer[17] and by Hill,[18] and more recently it has again been applied to barriers to internal rotation.[19,20] Lack of reliable force laws based on independent experimental results has been the major drawback in such calculations up to the present.

Force Laws.—The force laws for non-bonded halogen atoms have been taken by analogy from force laws between rare gas atoms. The interactions between two fluorine atoms have been taken to be the same as those between two isolated neon atoms, and the interactions between chlorine atoms to be those between argon atoms. No use has been made of bromine and iodine interactions, but these are available by analogy with krypton[21–23] and xenon.[21,23,24] The halogen atoms in a molecule

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[4] R. W. Taft, Jr., THIS JOURNAL, **75**, 4538 (1953).

[5] H. C. Brown and R. M. Horowitz, *ibid.*, **77**, 1733 (1955); see also references quoted in these papers.

[6] (a) K. S. Pitzer, *Disc. Faraday Soc.*, **10**, 66 (1951); (b) K. S. Pitzer, *ibid.*, **10**, 124 (1951).

[7] C. A. Coulson, "Valence," Oxford at the Clarendon Press, London, England, 1952, pp. 314–317.

[8] (a) H. Eyring, THIS JOURNAL, **54**, 3191 (1932); (b) E. Gorin, J. Walter and H. Eyring, *ibid.*, **61**, 1876 (1939).

[9] (a) E. N. Lassettre and L. B. Dean, *J. Chem. Phys.*, **16**, 151 (1948); (b) **16**, 553 (1948); (c) **17**, 317 (1949).

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[12] F. A. French and R. S. Rasmussen, *ibid.*, **14**, 389 (1946).

[13] H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).

[14] T. Simanouti, *J. Chem. Phys.*, **17**, 848 (1949).

[15] D. F. Heath and J. W. Linnett, *ibid.*, **18**, 147 (1950).

[16] (a) G. L. Lewis and C. P. Smyth, *ibid.*, **7**, 1085 (1939); (b) A. Di Giacomo and C. P. Smyth, THIS JOURNAL, **77**, 1361 (1955).

[17] (a) F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.*, **14**, 733 (1946); (b) F. H. Westheimer, *ibid.*, **15**, 252 (1947); (c) M. Rieger and F. H. Westheimer, THIS JOURNAL, **72**, 19 (1950).

[18] T. L. Hill, *J. Chem. Phys.*, **16**, 938 (1948), and previous papers.

[19] J. van Dranen, *ibid.*, **20**, 1982 (1952).

[20] N. W. Luft, *ibid.*, **22**, 1814 (1954).

[21] E. A. Mason and W. E. Rice, *ibid.*, **22**, 843 (1954).

[22] I. Amdur and E. A. Mason, *ibid.*, in press.

[23] E. Whalley and W. G. Schneider, *ibid.*, **23**, 1644 (1955).

[24] I. Amdur and E. A. Mason (to be published).

have the same number of electrons but a nuclear charge smaller by one unit than the corresponding rare gas atoms, and might therefore be expected to exhibit somewhat larger repulsive forces than the rare gas atoms. In a molecule, however, the electron cloud is drawn somewhat into the bond, thus tending to make the repulsive forces smaller. These two effects act in opposite directions and tend to compensate each other. We have assumed that the compensation is complete, and have ignored both effects.

Analysis of second virial coefficients and transport properties of gases leads to laws of force which can be considered valid for comparatively large distances of separation of the particles; for information at smaller separation distances, the results of experiments on the scattering of beams of high velocity neutral particles in room temperature gases have been used. The scattering experiments give information as to the forces at small separation distances, but not at large distances. Thus the complete intermolecular potential energy function to be used is represented piecewise in different regions. Equations 1 and 2 show the potential functions used for fluorine–fluorine and chlorine–chlorine interactions, respectively. Equation 1 is derived from data on neon and eq. 2 from data on argon. The quantity $\varphi(r)$ is the potential energy in kcal./mole between two atoms at a separation distance of r Ångströms.

F–F

$$\varphi(r) = (7.20 \times 10^3)/r^{9.99} \qquad (1.76\ \text{Å.} \leqq r \leqq 2.3\ \text{Å.})^{25} \quad \text{(1a)}$$

$$\varphi(r) = (1.057 \times 10^3) \exp(-4.608r) - 125.1/r^6 \qquad (r \geqq 2.3\ \text{Å.})^{21} \quad \text{(1b)}$$

Cl–Cl

$$\varphi(r) = (1.300 \times 10^4)/r^{7.87} \qquad (2.18\ \text{Å.} \leqq r \leqq 3.0\ \text{Å.})^{26} \quad \text{(2a)}$$

$$\varphi(r) = (2.208 \times 10^5) \exp(-3.621r) - (1.430 \times 10^3)/r^6 \quad (r \geqq 3.0\ \text{Å.})^{21} \quad \text{(2b)}$$

In the molecules under discussion the halogen atoms may carry a substantial negative charge. We have assumed that this charge could be treated as a point charge located at the center of the atom and obeying Coulomb's law. Thus eq. 1 and 2 need to be modified by the addition of a coulomb term in $1/r$. The magnitudes of the partial negative charges in various compounds have been calculated whenever possible by the method of Smith, Ree, Magee and Eyring,[27] in which partial charges are distributed on the constituent atoms of a molecule in accordance with accepted bond polarizabilities, screening constants, covalent bond radii and electric dipole moments. When insufficient data were available for such a calculation, the partial charges were determined by dividing the bond dipole moment by the bond length, a procedure which gives nearly the same result. In any case, only a rough estimate of the charge is needed, since the contribution of the coulomb interactions to the calculated barrier is rather small. In the most extreme case (hexafluoroethane), the calculated contribution to the barrier from the coulomb repulsions was only 0.2 kcal./mole, about 10% of the total calculated barrier. The reason for the small contribution of the coulomb term is of course the slow variation of the potential energy with distance. The energy difference between a staggered and an eclipsed configuration of an ethane-like molecule is much less for the coulomb repulsion than for the ordinary van der Waals repulsion energy.

In the case of interactions between two non-bonded hydrogen atoms, no experimental intermolecular potentials are known. The system He–He seemed to be a poor model because the nuclear charge of helium is twice that of hydrogen. It was therefore assumed that the appropriate force law would be similar to that governing the interactions between two isolated non-bonding hydrogen atoms (the $^3\Sigma$ state of H_2). That is, the appropriate potential could be represented as $K\varphi(r)$, where K is a constant and $\varphi(r)$ is the potential energy function for $^3\Sigma\ H_2$. Rather accurate values of $\varphi(r)$ have been calculated by Hirschfelder and Linnett,[28] and eq. 3 was derived by curve-fitting their results

$$\varphi(r) = (3.7164 \times 10^3) \exp(-3.0708r) - 89.52/r^6 \qquad (r \geqq 1.8\ \text{Å.}) \quad (3)$$

where $\varphi(r)$ is in kcal./mole and r in Å.

The proper value of K to be used is subject to some uncertainty. Simple valence bond theory would predict a value of about 0.5 for K.[8a,29] Such a value has been used,[30] and seems to underestimate the repulsion energy. The valence bond approximation further neglects the additional repulsion of the C–H bond electron pairs in the region of the C atoms, which probably has an appreciable effect on the barrier.[6a] Thus the effect of bonding is to decrease the repulsion between the H atoms themselves, but increase the repulsion due to the C–H bonds. Since neither effect can be accurately calculated, we have assumed a compensation and taken $K = 1.0$. This is undoubtedly an upper limit, and $K = 0.5$ a lower limit. Some recent rough calculations by van Dranen[19] seem to favor the larger value. Equation 3 should represent a considerable improvement over the potential used earlier by Eyring.[8a] Even if K is taken as 0.5, the barrier calculated for ethane is over twice that calculated by Eyring.

Interactions involving methyl groups have been treated in two ways. The first method involves adding up the contributions for all the pairs of hydrogen atoms according to eq. 3, neglecting the effects of the central carbon atoms as originally suggested by Aston, *et al.*[11] The second method, which is much the easier to apply in any particular case, makes use of an average methyl–methyl interaction as determined by analogy with the potential energy between two methane molecules. These average interaction energies, in kcal./mole, are

$$\varphi(r) = (2.390 \times 10^4)/r^{7.37} \qquad (2.47\ \text{Å.} \leqq r \leqq 3.2\ \text{Å.})^{31} \quad \text{(4a)}$$

$$\varphi(r) = (2.739 \times 10^5) \exp(-3.329r) - (2.942 \times 10^3)/r^6 \quad (r \geqq 3.2\ \text{Å.})^{21} \quad \text{(4b)}$$

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(25) I. Amdur and E. A. Mason, *J. Chem. Phys.*, **23**, 415 (1955).

(26) I. Amdur and E. A. Mason, *ibid.*, **22**, 670 (1954).

(27) R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

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(29) J. de Boer, *Physica*, **9**, 363 (1942).

(30) H. O. Pritchard and F. H. Sumner, *J. Chem. Soc.*, 1041 (1955).

Equation 4a was determined indirectly from measurements on the scattering of high velocity beams of argon atoms in room temperature methane gas,[31] and eq. 4b was determined from gas and crystal properties.[21] The value of r refers to the distance between the carbon atoms of the methyl groups.

The potentials between pairs of unlike atoms or groups can be obtained from the potentials between the appropriate pairs of like atoms or groups as given by eq. 1–4 by means of combination rules, and then a coulomb repulsion term added, if necessary, as discussed above. Suitable combination rules for these types of potentials have been developed, and consist essentially of taking geometric means of the corresponding terms in the potentials between like pairs.[32,33]

Results

From the geometry of an ethane-like molecule and the forces between its non-bonded atoms, it is a straightforward if somewhat tedious procedure to calculate the complete barrier to internal rotation. For the sake of consistency we have included all possible interactions in our calculations (a total of nine H–H interactions in ethane itself, for example), although the interactions at the larger distances contribute but little to the barrier. Barriers for a total of 31 molecules not complicated by rotational isomerism have been calculated for comparison with experimentally determined barrier heights. Since the calculated barriers are sensitive to the bond distances and angles, the values used for these structural parameters are listed in Table I. In some cases, where structural parameters were known with accuracy, such parameters have been used directly, but for the most part, commonly accepted values of bond angles and distances have been taken. The barrier height V_0 has been calculated directly as

$$V_0 = V(\text{eclipsed}) - V(\text{staggered}) \qquad (5)$$

The major contribution to V_0 comes from differences between values of $\varphi(r)$ for which the values of r do not differ by much; that is, the barrier height depends largely on the rate of variation of $\varphi(r)$ with r, rather than on the value of $\varphi(r)$ itself. This fact throws considerable strain on the accuracy of the present calculations, since the experimental methods used to obtain $\varphi(r)$ tend to yield values of $\varphi(r)$ itself rather than its variation with r directly. This is especially evident in the regions where two different analytical representations of the complete $\varphi(r)$ curve meet, such as the region around 3.0 Å. for Cl–Cl, as given by eq. 2.

The shape as well as the height of the barrier to rotation is of importance. In most cases $V_0 > RT$, so that it is the shape of the barrier near the minimum which is important, since this shape determines the spacing of the first few energy levels for torsional oscillation and it is just these levels which have the most influence on the measurable quantities from which experimental barrier heights are determined. In view of the lack of any definite knowledge about barrier shapes in most molecules, it has been customary to select for the interpretation of experimental results the cosine potential

$$V(\theta) = (1/2)\,V_0'(1 - \cos n\theta) \qquad (6)$$

where V_0' is the barrier height, a constant to be determined by comparison with experimental results.

TABLE I

VALUES OF STRUCTURAL PARAMETERS USED

Substance	Structural parameters	Ref.
CH_3CH_3	CC 1.543; CH 1.102; ∠CCH 109° 37′	*a*
CH_3SiH_3	CSi 1.857; CH 1.09; SiH 1.48; ∠s tetr.	*b*
SiH_3SiH_3	SiSi 2.32; SiH 1.47; ∠s tetr.	*c*
$CH_3C{\equiv}CCH_3$	CC 1.460; C≡C 1.207; CH 1.097; ∠s tetr.	*d*
CH_3OH	CO 1.459; CH 1.093; OH 0.854; ∠OCH 109° 28′; ∠COH 109° 3′	*e*
CH_3SH	CS 1.815; CH 1.102; SH 1.334; ∠SCH 109° 28′; ∠CSH 100°	*f*
CH_3NH_2	CN 1.469; CH 1.093; NH 1.01; ∠NCH 109° 28′; ∠CNH 108°	*g*
$C_6H_5CH_3$	CC (Me) 1.543; CC (Ph) 1.40; CH (Me) 1.093; CH (Ph) 1.04; ∠CCH (Me) 109° 28′; ∠CCH (Ph) 120°	*h*
NH_2NH_2	NN 1.47; NH 1.04; ∠s tetr.	*i*
CF_3CF_3	CC 1.543; CF 1.330; ∠s tetr.	*j*
$CF_3C{\equiv}CCF_3$	CC 1.465; C≡C 1.22; CF 1.340; ∠s tetr.	*k*
CCl_3CCl_3	CC 1.55; CCl 1.74; ∠s tetr.	*l*
$SiCl_3SiCl_3$	SiSi 2.34; SiCl 2.02; ∠s tetr.	*m*
BCl_2BCl_2	BB 1.75; BCl 1.73; ∠ClBCl, ∠BBCl 120°	*n*
CF_3SF_5	CS 1.86; CF 1.33; SF 1.57; ∠SCF 109° 28′; ∠CSF 90°; ∠FSF 90°	*o*
CH_3CF_3	CC 1.54; CH 1.093; CF 1.33; ∠s tetr.	*p*
CH_3SiF_3	CSi 1.88; CH 1.10; SiF 1.555; ∠s tetr.	*q*
$CH_3C{\equiv}CCF_3$	CF 1.330; others as in $CH_3C{\equiv}CCH_3$	
CH_3CCl_3	CC 1.54; CH 1.093; CCl 1.767; ∠s tetr.	*r*
CH_3CH_2F CH_3CHF_2	Calculations based on C_2H_6 and C_2F_6.	
CH_3CH_2Cl	Calculations based on C_2H_6 and CH_3CCl_3.	
CF_3CF_2Cl	CC 1.543; CF 1.330; CCl 1.77; ∠s tetr.	*j, r*
$CH_3CH_2(CH_3)$ $CH_3CH(CH_3)_2$ $CH_3C(CH_3)_3$	CC 1.54; CH 1.102; ∠s tetr.	
$CH_3Si(CH_3)_3$	CSi 1.888; CH 1.102; ∠s tetr.	*s*
CH_3OCH_3	CO 1.42; CH 1.093 (as in CH_3OH); ∠s tetr.	*t*
CH_3SCH_3	CS 1.82; CH 1.102 (as in CH_3SH); ∠SCH 109° 28′; ∠CSC 105°	*t, u*
$CH_3NH(CH_3)$ $CH_3N(CH_3)_2$	Same as CH_3NH_2; ∠CNC, ∠CNH 108°	

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TABLE II

COMPARISON OF CALCULATED AND OBSERVED BARRIERS TO INTERNAL ROTATION FOR SOME SIMPLE MOLECULES

Substance	Calcd., kcal./mole V_0	$V_{\cos}$	Exptl., kcal./mole V_0'	Ref.
CH_3CH_3	1.77	1.72	2.875 ± 0.125	*a*
CH_3SiH_3	0.51	0.50	1.314 ± 0.229	*b*
SiH_3SiH_3	0.10	0.10	Appreciable	*c*
$CH_3C{\equiv}CCH_3$	0.000	0.000	0	*d*
CH_3OH	0.72	0.71	1.07	*e*
CH_3SH	0.50	0.48	1.06 ± 0.12	*f*
			0.80 ± 0.14	*g*
CH_3NH_2	1.71	1.67	1.94	*h*
			1.80	*i*
			1.90	*j*
$C_6H_5CH_3$	0.07	0.07	0.5 ± 0.5	*k*
NH_2NH_2	2.71	...	2.80	*l*
CF_3CF_3	2.14	1.88	3.92	*m*
$CF_3C{\equiv}CCF_3$	0.004	0.004	Free rot.	*n*
			Staggered	*o*
CCl_3CCl_3	9.19	15.66	$\geqq 7 \pm 1$	*p*
$SiCl_3SiCl_3$	0.39	0.30	Nearly free	*q*
BCl_2BCl_2	0.64	0.27	1.53 ± 0.60	*r*
CF_3SF_5	0.00	0.00	0.63 ± 0.32	*s*
CH_3CF_3	2.14	2.01	3.25 ± 0.40	*t*
			3.29	*u*
			3.35 ± 0.12	*v*
			3.66	*w*
CH_3SiF_3	0.36	0.34	1.20 ± 0.16	*x*
$CH_3C{\equiv}CCF_3$	0.000	...	Small	*y*
CH_3CCl_3	1.83	4.87	2.97	*z*
CH_3CH_2F	1.90	1.82	3.96	*w*
			4.26 ± 0.15	*aa*
CH_3CHF_2	2.02	1.92	3.95	*w*
			3.57 ± 0.58	*bb*
CH_3CH_2Cl	1.79	2.77	2.7	*cc*
			4.7	*dd*
			3.0	*ee*
CF_3CF_2Cl	2.81	2.61	5.3	*ff*

[a] K. S. Pitzer, *Disc. Faraday Soc.*, 10, 66 (1951). [b] D. R. Lide and D. K. Coles, *Phys. Rev.*, **80**, 911 (1950). [c] H. S. Gutowsky and E. O. Stejskal, *J. Chem. Phys.*, **22**, 939 (1954). [d] D. W. Osborne, C. S. Garner and D. M. Yost, *ibid.*, **8**, 131 (1940); I. M. Mills and H. W. Thompson, *Proc. Roy. Soc.* (*London*), **A226**, 306 (1954). [e] E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, 22, 1804 (1953). [f] N. Solimene and B. P. Dailey, *ibid.*, **23**, 124 (1955). [g] T. Kojima and T. Nishikawa, *J. Phys. Soc. Japan*, **10**, 240 (1955). [h] K. Shimoda, T. Nishikawa and T. Itoh, *J. Chem. Phys.*, 22, 1456 (1954); *J. Phys. Soc. Japan*, **9**, 974 (1954). [i] D. R. Lide, *J. Chem. Phys.*, **22**, 1613 (1954). [j] J. G. Aston and F. L. Gittler, *ibid.*, **23**, 211 (1955). [k] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943). This barrier has six maxima and minima. [l] D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, *ibid.*, 71, 2293 (1951). No value of $V_{\cos}$ is given because our simple model does not predict a minimum for this molecule where one actually exists. [m] D. E. Mann and E. K. Plyler, *J. Chem. Phys.*, 21, 1116 (1953). [n] W. F. Sheehan and V. Schomaker, THIS JOURNAL, **74**, 4468 (1952). [o] F. A. Miller and R. P. Baumann, *J. Chem. Phys.*, 22, 1544 (1954). [p] D. A. Swick, I. L. Karle and J. Karle, *ibid.*, 22, 1242 (1954). [q] K. Yamasaki, A. Kotera, A. Tatematsu and M. Iwasaki, *J. Chem. Soc. Japan*, **69**, 104 (1947); M. Katayama, T. Simanouti, Y. Morino and S. Mizushima, *J. Chem. Phys.*, 18, 506 (1950). [r] M. J. Linevsky, Thesis Penna. State Univ. (1953). [s] P. Kisiuk and G. A. Silvey, *J. Chem. Phys.*, **20**, 517 (1952). This barrier has twelve maxima and minima. [t] H. W. Thompson and R. B. Temple, *J. Chem. Soc.* (*London*), 1428 (1948). [u] J. R. Nielsen, H. H. Claassen and D. C. Smith, *J. Chem. Phys.*, 18, 1471 (1950). [v] H. T. Minden and B. P. Dailey, *Phys. Rev.*, **82**, 338 (A) (1951); B. P. Dailey, *Ann. N. Y. Acad. Sci.*, **55**, 915 (1952). [w] D. C. Smith, R. A. Saunders, J. R. Nielsen and E. E. Ferguson, *J. Chem. Phys.*, **20**, 847 (1942). [x] H. T. Minden, J. M. Mays and B. P. Dailey, *Phys. Rev.*, **78**, 347 (A) (1950); H. T. Minden and B. P. Dailey, *ibid.*, **82**, 338 (A) (1951); J. Sheridan and W. Gordy, *J. Chem. Phys.*, 19, 965 (1951). [y] B. Bak, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, 21, 1612 (1953). [z] K. S. Pitzer and J. L. Hollenberg, THIS JOURNAL, **75**, 2219 (1953). [aa] J. Kraitchman and B. P. Dailey, *J. Chem. Phys.*, **23**, 184 (1955). [bb] N. Solimene and B. P. Dailey, *ibid.*, 22, 2042 (1954). [cc] A. Eucken and E. U. Franck, *Z. Elektrochem.*, 52, 195 (1948). [dd] J. Gordon and W. F. Giauque, THIS JOURNAL, **70**, 1506 (1948). [ee] R. S. Wagner and B. P. Dailey, *J. Chem. Phys.*, 22, 1459 (1954). [ff] J. G. Aston and T. P. Zolki, THIS JOURNAL, **77**, 804 (1955).

Blade and Kimball[34] have considered other shapes, but available evidence[6a,35] seems rather to confirm the cosine shape of eq. 6. It is, therefore, important to know whether the barriers calculated from our force laws are representable with any precision by a cosine potential. Rather than calculate the the complete $V(\theta)$ curves, we have determined the height of the cosine potential, $V_{\cos}$, which has same curvature at the minimum as our calculated $V(\theta)$ curves. It is this curvature which primarily determines the spacing of the first few energy levels for torsional oscillation. The relation between $V_{\cos}$ and the curvature is given by eq. 7

$$V_{\cos} = \frac{2}{n^2}\,\frac{d^2V(\theta)}{d\theta^2} \tag{7}$$

where n is the number of minima, as in eq. 6, and the second derivative is to be evaluated from our force laws at a value of θ for which $V(\theta)$ is a minimum. The value of $V_{\cos}$ is perhaps a more significant quantity than V_0, since the lowest energy levels have the most influence on measurable properties when $V_0 > RT$. The agreement between our calculated values of V_0 and $V_{\cos}$ is thus a measure of the closeness of the barrier to the cosine shape.

Table II contains a comparison, for molecules in which only simple non-bonded atoms interact to form a rotational barrier, of the calculated values of V_0 and $V_{\cos}$ and the experimentally determined values of V_0'. The agreement between V_0 and $V_{\cos}$ is usually good, indicating that the cosine potential is a good approximation, in agreement with recent analyses of experimental results.[6a,35] The outstanding exceptions are those molecules in which interactions involving chlorine atoms are important. This disagreement is partly due to the fact that in these cases the uncertain transition region between the $\varphi(r)$ potentials as determined from scattering data and from gas and crystal properties data is involved in the barrier calculations. Although the two expressions for the potential join properly, their slopes do not join well. For instance, in the case of CH_3CCl_3 if eq. 2b for $\varphi(r)$ had been extrapolated to small values of r rather than use eq. 2a, the value of V_0 would have been 5.24 kcal./mole. This is in fair agreement with the value of $V_{\cos}$, whose value is not influenced by eq. 2b. It should be mentioned that in most cases considerable uncertainty also exists in the values of V_0', the experimental barrier heights, since they may depend es-

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sentially on the small difference between two large quantities, the spectroscopic and the thermodynamic entropies or heat capacities. More detailed consideration of the errors involved can be found elsewhere.[36,37] Barriers determined by the use of microwaves should have greater accuracy than those determined from thermodynamic properties, but in many cases the uncertainties in the detailed interpretation of the observed spectrum to obtain the barrier height may lead to error. The most accurately known barriers are probably those for ethane and methanol.

In Table III are listed the results for molecules in which methyl groups interact. As mentioned previously, two methods of calculation have been employed, the first involving hydrogen atom interactions and the second using the average methyl group potential energy functions given in eq. 4. The barriers calculated by the second method are denoted by the subscript "av." The barriers calculated by the first method are the minimum values to be expected, since it has been assumed that the methyl groups hindering rotation maintain angles of minimum interaction throughout the rotation. This situation has been termed "perfect cogwheeling" by Pitzer and Scott.[38] Figure 1 illustrates the situation for propane, and shows the staggered configuration of minimum energy and two opposed configurations, one of which has the lowest possible energy for an opposed configuration and the other of which has the highest possible energy for an opposed configuration. The maximum opposed energy is calculated to be some 6.5 kcal./mole higher than the minimum opposed energy, which in turn is only about 2 kcal./mole higher than the minimum staggered energy. It is this last figure which we have taken as the barrier height, so it is not surprising that the calculated barriers are substantially lower than the experimental ones, inasmuch as higher energy configurations may contribute to the experimental barrier values.

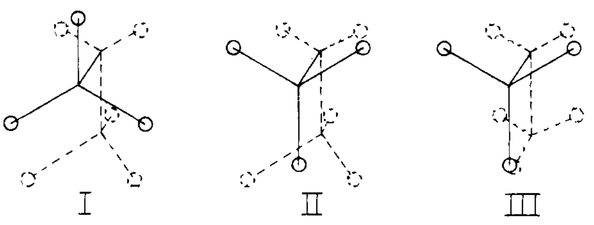

Fig. 1.—Minimum staggered (I), minimum opposed (II), and maximum opposed (III) configurations for propane. Symmetry considerations require that these three configurations be either minima or maxima in the plots of $V(\theta)$ *vs.* angle of rotation of either methyl group, since rotation in either direction produces identical configurations. The energy of II is calculated to be about 2 kcal./mole higher than I whereas III is 6.5 kcal./mole higher than II.

TABLE III

COMPARISON OF CALCULATED AND OBSERVED BARRIERS TO INTERNAL ROTATION FOR SOME MOLECULES INVOLVING METHYL GROUP INTERACTIONS

	Calcd., kcal./mole			Exptl., kcal./mole	
Substance	$<V_0>_{av}$	V_0	V_{cos}	V_0'	Ref.
$CH_3CH_2(CH_3)$	1.78	1.92	1.79	3.30	*a*
				3.40	*b*
$CH_3CH(CH_3)_2$	1.78	2.00	1.79	3.87	*c*
				3.62	*d*
$CH_3C(CH_3)_3$	1.78	2.08	1.80	4.30	*e*
$CH_3Si(CH_3)_3$	1.95	0.60	0.62	1.3 ± 0.2	*f*
CH_3OCH_3	4.12	1.06	1.42	2.70	*g*
				3.00	*h*
CH_3SCH_3	1.49	0.54	0.60	2.00	*i*
$CH_3NH(CH_3)$	4.53	1.72	2.47	3.46	*j*
$CH_3N(CH_3)_2$	7.34	1.73	3.28	4.27	*k*

[a] G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **8**, 610 (1940). [b] K. S. Pitzer, *ibid.*, **12**, 310 (1944). [c] J. G. Aston, R. M. Kennedy and S. C. Schumann, THIS JOURNAL, **62**, 2059 (1940). [d] K. S Pitzer and J. E. Kilpatrick, *Chem. Revs.*, **39**, 435 (1946). [e] J. G. Aston and G. H. Messerly, THIS JOURNAL, **58**, 2354 (1936); also ref. *d* above. [f] J. G. Aston, R. M. Kennedy and G. H. Messerly, *ibid.*, **63**, 2343 (1941). [g] R. M. Kennedy, M. Sagenkahn and J. G. Aston, *ibid.*, **63**, 2267 (1941); F. A. French and R. S. Rasmussen, *J. Chem. Phys.*, **14**, 389 (1946). [h] A. Eucken and E. U. Franck, *Z. Elektrochem.*, **52**, 195 (1948). [i] D. W. Osborne, R. N. Doescher and D. M. Yost, THIS JOURNAL, **64**, 169 (1942). [j] J. G. Aston, M. L. Eidinoff and W. S. Forster, *ibid.*, **61**, 1539 (1939). [k] J. G. Aston, M. L. Sagenkahn, G. J. Szasz, G. W. Moessen and H. F. Zuhr, *ibid.*, **66**, 1171 (1944).

It is seen that the barriers calculated from the average methyl interaction are usually in fair agreement with the more elaborate calculations, so that nearly as good results often can be expected with average methyl potentials with a good deal less computation. The inconsistencies in the results of the calculation with average potentials, such as a higher barrier in $CH_3Si(CH_3)_3$ than in $CH_3C(CH_3)_3$, are due to the uncertain transition region in the potentials, in a manner similar to that for the chlorine interactions mentioned previously. Because of this uncertainty, only the barrier heights, $<V_0>_{av.}$, have been calculated from the average potentials.

Discussion

Although the uncertainties in the calculated barriers and in many of the experimental barriers are rather large, it is gratifying that the van der Waals repulsions account for a major portion of the barrier height in most cases. In this connection, it is worth emphasizing that the present calculations involve no disposable parameters. A rigorous estimate of the possible error involved in the calculations is difficult to make, because the model is so drastically simplified. The ultimate justification of the procedure we have used must come empirically from comparing model calculations with experimental results, as we have attempted to do in the present paper.

The remainder of the barrier heights can perhaps be attributed to the electrostatic interactions between the charge distributions of the bonds.[3,9] For example, in the case of ethane, use of the bond quadrupole moment calculated by Lassettre and Dean[9b,9c] by a molecular orbital method and somewhat smaller than the value required to account for the whole barrier,[9c] is sufficient to give good agreement with the experimental barrier height. This suggestion is also supported by the fact that the

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[38] K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 803 (1943).

agreement between calculated and observed barriers is best in those cases where the internuclear distances involved are smallest. Multipole interactions, dipole–dipole, dipole–quadrupole and quadrupole–quadrupole, fall off less rapidly with distance than do van der Waals repulsions, so that the van der Waals forces would be expected to be relatively more important at small internuclear distances. The uncertainties in bond moments are such[3,10] that the above must be considered only speculation, however.

The model used in the present investigation is highly simplified, and a number of effects have been ignored which should be taken into account in a more rigorous treatment. Two effects which may be important are deformation of the bond angles and interactions of atoms with unshared pairs of electrons on other atoms. These latter occur in methanol and the various methylamines. Nevertheless, the model seems capable of giving semi-quantitative results and it is hoped that the force laws for interactions between non-bonded atoms given in this paper will prove useful in the calculation of other types of steric effects.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Iodide–Iodine–Triiodide Equilibrium and Ion Activity Coefficient Ratios[1]

BY LEONARD I. KATZIN AND ELIZABETH GEBERT

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The triiodide dissociation constant is determined at 20, 25 and 30° by measuring the solubility of iodine in iodide solutions. It is demonstrated that the activity coefficient ratio of iodide and triodide ions in the same solution is a function of solution composition, and the differences between different media are greater at higher ionic strengths. Entropy data for the three reactions, $X^- + I_2 \cdot H_2O = XI_2^- + H_2O$ are shown to be consistent with this formulation.

A recent spectrophotometric study of the iodide–iodine–triiodide equilibrium[2] seemed to indicate that in 1 *M* acid the stability of the triiodide is greater at higher temperature than at lower, a reversal of the temperature coefficient determined by other techniques[3,4] for non-acid solutions. Verification by other methods seemed required. The approach chosen was the measurement of the change in solubility of iodine in water as a function of potassium or sodium iodide concentration. With the activity of the iodine fixed by the presence of solid phase, the increased iodine content is a direct measure of the triiodide formed in a solution of known total iodide concentration. This paper presents the findings of experiments using this technique.

Experimental

The equilibration vessels used were 125-ml. glass-stoppered erlenmeyer flasks sealed with paraffin. They were shaken in a commercial shaking device in air for several hours, then transferred to a less efficient form of shaker mounted in a constant temperature water-bath, whose temperature was fixed to ±0.15°. Solutions containing iodide came to apparent equilibrium in 24 hours; solutions without iodide added changed slowly in iodine concentration over periods up to a week in length. This period was shorter at higher perchloric acid concentrations.

Three series of solutions, containing 1 *M*, 0.01 *M* and no added perchloric acid were investigated at three temperatures, 20, 25 and 30°. Effects of ionic strength as such were tested using sodium perchlorate. When a solution was to contain KI or NaI, the solid C.P. salt was weighed out and made up to 100 ml. with the appropriate addition of 1 *M* stock sodium perchlorate and perchloric acid solutions. The resulting solutions were then transferred to the equilibration flasks together with excess solid sublimed iodine, and the flasks were sealed.

When equilibration was completed, aliquots were pipetted through glass wool filters and titrated with thiosulfate solution. The latter was standardized daily against potassium iodate, using the iodate–iodide reaction,[5] and starch indicator end-point. The end-points of iodine solutions not containing iodide were found to be sharpened considerably by adding KI to the titration flask; the starch–triiodide color was considerably more intense than the simple starch–iodine color.

Iodine Solubility.—The solubility of iodine was determined in water and the several base solutions to be used in the experiments. The average values found in a series of determinations are given in Table I. Our determination of the solubility of iodine in water at 25° agrees quite satisfactorily with the consensus of the literature determinations.[6–17] At 20 and 30° there is good agreement with the values read from a composite plot of the published solubilities over a temperature range.[18] The water equilibria to give oxyiodine products are apparently not sufficient to

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

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