in magneto-optical rotation spectra at the absorption band regions of molecules. Moreover, the shapes of the dispersion curves are defined by five types rather than the two characteristic Cotton effects[25] of natural optical activity measurements. In addition, the type of m.o.r. spectrum obtained is characteristic of particular transition rather than the molecule as a whole. The experimental observations studied so far indicate that m.o.r.

(25) A. Cotton, *Compt. rend.*, **120**, 989 (1895).

spectroscopy may prove useful for studying molecular structure and configuration.

A Method of Diatomics in Molecules. III. H₂X and X₂H (X = H, F, Cl, Br, and I)[1]

BY FRANK O. ELLISON AND JASHBHAI C. PATEL

Diatomics in molecules theory[2] is applied to the elementary reactions $H_2 + X = H + HX$ and $X_2 + H = X + HX$, where X = H, F, Cl, Br, or I, for linear configurations only. The combined three-atom systems are represented by a resonance of the two canonical structures A–B C and A B–C. The energy matrix elements can be expressed in terms of overlap matrix elements (for the polyatomic structures) and experimental ground and excited state energies of the diatomic and monatomic fragments. Hulburt–Hirschfelder potential curves are employed for diatomic ground states, approximate potentials are developed and used for diatomic excited states, and accurate curves are also used for H_2. Classical activation energies, which are in good agreement with accepted experimental values, bond energies, and optimum bond lengths are calculated. Uncertainties introduced by the use of approximate diatomic potential energy curves in diatomics in molecules theory are discussed.

In a previous paper,[2] a new approximate theory was developed for calculating the energy of a polyatomic molecule (for any fixed positions of the nuclei) in terms of empirical ground and excited state energies of all possible diatomic and monatomic fragments which comprise the polyatomic as well as all overlap integrals between valence-bond wave functions postulated to describe it. The theory contains two fundamental assumptions: (1) the electronic structure of a polyatomic molecule *can* be represented adequately by a reasonably limited set of canonical valence-bond structures; and (2) the ground and excited state eigenfunctions of all possible diatomic and monatomic fragments can be represented adequately by valence-bond wave functions built from appropriate subsets of the same atomic orbital basis set as employed in the total polyatomic description. No approximations of integrals and no adjustable parameters are necessary in the theory, although it has been noted that neglect of overlap integrals between atomic orbitals has little effect on the final energies.

Results of applications to H_2O, H_3, and H_3^+ are encouraging[2,3]; calculated molecular energies differ from experiment by only 1–2, 5, and possibly 6–10 kcal., respectively. In this paper, diatomics in molecules theory is applied to the systems H_2X and HX_2, where X = F, Cl, Br, or I. For these cases, one of the main stumbling blocks in applying the theory is met squarely, namely, that accurate potential energy curves for both ground and excited diatomic states are necessary ingredients. Since these are not available for HX and X_2, approximate curves are developed, and the theory also is reapplied to H_3, for which accurate calculations have already been made.[3]

(1) Supported in part by a grant from the National Science Foundation.

(2) F. O. Ellison, *J. Am. Chem. Soc.*, **85**, 3540 (1963), to be referred to as paper I.

(3) F. O. Ellison, N. T. Huff, and J. C. Patel, *ibid.*, **85**, 3544 (1963), to be referred to as paper II.

Previous semiempirical calculations on these systems as well as others include, for example, early applications of the London–Eyring–Polanyi method by Eyring[4] and Hirschfelder,[5] the modification thereof by Sato,[6] and a recent new procedure by Johnston and Parr.[7]

Theory

The reactions

$$H_2 + H \rightleftharpoons H + H_2 \qquad (1)$$

$$H_2 + X \rightleftharpoons H + HX \qquad (2)$$

$$X_2 + H \rightleftharpoons X + XH \qquad (3)$$
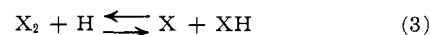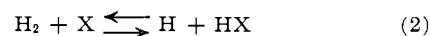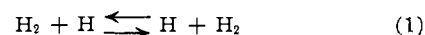
where X = F, Cl, Br, or I, may all be written as AB + C = A + BC. Linear configurations of the combined three-atom system ABC should be representable in the first approximation by resonance of two canonical structures A–B C and A B–C.

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \qquad (4)$$

$$\Psi_1 = |a\bar{b}c| - |\bar{a}bc|$$

$$\qquad\qquad\qquad\qquad (5)$$

$$\Psi_2 = |a\bar{b}c| - |ab\bar{c}|$$

If atom B is H, for example, then b represents a 1s orbital on that center; a bar over the orbital denotes β-spin, no bar means α-spin. If, on the other hand, atom B is Br, then b represents a 4p orbital on that center, and it is understood that the nonbonding $1s^2$-$2s^22p^63s^23p^64s^23d^{10}4p^4$ electron orbitals should also be written into the determinantal wave functions. In order to determine the optimum coefficients a_n for which the expectation value of the molecular energy

(4) H. Eyring, *ibid.*, **53**, 2537 (1931).

(5) J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

(6) S. Sato, *ibid.*, **23**, 592, 2465 (1955).

(7) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

W is minimized (for fixed internuclear distances R_{AB} and R_{BC}), one must solve the secular determinant $|H_{nm} - S_{nm}W| = 0$, in which $H_{nm} = \int \Psi_n H \Psi_m d\tau$ and $S_{nm} = \int \Psi_n \Psi_m d\tau$.

The diatomics in molecules evaluation of the H_{nm}, in terms of overlap integrals S_{nm} and experimental ground and excited states of all possible diatomic and monatomic fragments, is illustrated fully in that part of paper II which treats linear H_3.[3] The resulting equations may be summarized as

$$H_{nm} = \bar{H}_{nm}^{AB} + \bar{H}_{nm}^{AC} + \bar{H}_{nm}^{BC} -$$
$$\bar{H}_{nm}^{A} - \bar{H}_{nm}^{B} - \bar{H}_{nm}^{C} \quad (6)$$

$$\bar{H}_{nm}^{PQ} = \frac{1}{2}(H_{nm}^{PQ} + H_{mn}^{PQ}) \quad (7a)$$

$$\bar{H}_{nm}^{P} = \frac{1}{2}(H_{nm}^{P} + H_{mn}^{P}) \quad (7b)$$

$$H_{nm}^{PQ} = \int \Psi_n \mathcal{H}_{PQ} \psi_m d\tau \quad (8a)$$

$$H_{nm}^{P} = \int \Psi_n \mathcal{H}_P \psi_m d\tau \quad (8b)$$

$$\mathcal{H}_{AB}\psi_1 = E_1^{AB}\Psi_1 \quad (9a)$$

$$\mathcal{H}_{AC}\psi_1 = [E_1^{AC}(\Psi_1 - \Psi_2) +$$
$$E_2^{AC}(\Psi_1 + \Psi_2)]/2 \quad (9b)$$

$$\mathcal{H}_{BC}\psi_1 = [E_1^{BC}\Psi_2 + E_2^{BC}(2\Psi_1 - \Psi_2)]/2 \quad (9c)$$

$$\mathcal{H}_{AB}\psi_2 = [E_1^{AB}\Psi_1 + E_2^{AB}(2\Psi_2 - \Psi_1)]/2 \quad (9d)$$

$$\mathcal{H}_{AC}\psi_2 = [E_1^{AC}(\Psi_2 - \Psi_1) +$$
$$E_2^{AC}(\Psi_1 + \Psi_2)]/2 \quad (9e)$$

$$\mathcal{H}_{BC}\psi_2 = E_1^{BC}\Psi_2 \quad (9f)$$

$$\mathcal{H}_P\psi_n = E_1^P\Psi_n, \; P = A, B, C \quad (10)$$

The E_1^{PQ} and E_2^{PQ} are *ground singlet* and *excited triplet* eigenvalues, respectively, for the diatomic fragment PQ, the internuclear distance of which corresponds to R_{PQ} in the total system ABC; E_1^P is the ground state eigenvalue for atom P.

Any integral H_{nm}^{PQ} may be evaluated easily in terms of overlap integrals S_{nm} and experimental ground and excited state energies of the diatomic fragment PQ by multiplying the appropriate eq. 9 by Ψ_n from the left and integrating; for example

$$H_{21}^{BC} = \int \Psi_2 \mathcal{H}_{BC}\psi_1 d\tau$$
$$= [E_1^{BC}S_{22} + E_2^{BC}(2S_{21} - S_{22})]/2 \quad (11)$$

In the three diatomics in molecules calculations performed to date (H_2O, H_3, and H_3^+), energy results obtained when overlap between atomic orbitals is included did not differ significantly (less than 0.4 kcal.) from those obtained when overlap between atomic orbitals is neglected. In all calculations reported in this paper, overlap between atomic orbitals is neglected; hence, overlap integrals between structures simplifies to $S_{11} = S_{22} = 2$ and $S_{12} = S_{12} = 1$.

It has been shown in paper I that diatomics in molecules theory leads directly to an expression for the atomization energy of a polyatomic as a sum of bond energies B_{PQ} (over "bonds" and "nonbonds") less the atomic promotional energy. For the triatomic molecule ABC, this expression is simply

$$\Delta E_{at} = B_{AB} + B_{BC} + B_{AC} - P_A - P_B - P_C \quad (12)$$

where

$$B_{PQ} = \sum_n \sum_m a_n a_m (\bar{H}_{nm}^{P} + \bar{H}_{nm}^{Q} - \bar{H}_{nm}^{PQ}) \quad (13)$$

$$P_P = \sum_n \sum_m a_n a_m \bar{H}_{nm}^{P} - E_P^\circ \quad (14)$$

in which the a_n are the optimum coefficients in eq. 4 chosen so that W is minimized and so that Ψ is normalized; E_P° ($= E_1^P$) is the ground state energy of atom P. In this work, none of the atoms are promoted, so $P_A = P_B = P_C = 0$.

Application

In order to apply the above theory to reactions 1–3, ground singlet state as well as excited triplet state potential energy curves for H_2, X_2, and HX are needed. Very accurate theoretically computed curves[8] as well as empirical Rydberg–Klein–Rees curves[9] are available for H_2, and these were utilized in the calculations on H_3 reported in paper II. For X_2 and HX (as well as for most other diatomics), no comparable data are available, and we must turn to more approximately formulated potential energy curves.

For ground singlet states, one of the best is the Hulburt–Hirschfelder curve, which has been adequately tested and fully described by Steele, *et al.*[9] The molecular properties entering this formulation as parameters are compiled in Table I. For the F_2 molecule, extrapolation was necessary to obtain values of $\omega_e x_e$, B_e, and α_e. Such extrapolations of molecular properties down to first row elements is oftentimes dangerous (*e.g.*, D_e); for the three properties mentioned, similar extrapolations in groups IV, V, and VI are quite valid, and there is no reason why extrapolations in group VII should be an exception.

For the excited triplet states of X_2 and HX, molecular data needed for constructing potential energy curves are not available. Since the final polyatomic molecule energies should be *relatively* insensitive to diatomic excited state energies, a simple scheme was devised for approximating these potentials. In elementary valence bond theory, the ground singlet and excited triplet energies (relative to separate atoms) for the equilibrium internuclear distance R_e are given by the equations

$$E_{1e} = J + K$$
$$\quad (15)$$
$$E_{2e} = J - K$$

where J and K represent coulomb and exchange energy, respectively. It has often been assumed in the past that the total binding energy E_{1e} is approximately 12–15% coulombic; however, Fraga and Mulliken have demonstrated that this percentage can and often is much higher.[10] We have taken $J = pE_{1e}$, and considered values of the paramater p from about 0.1 to about 0.4. Substituting this expression into eq. 15 gives

$$E_{2e} = E_{1e}(2p - 1) \quad (16)$$

For a given value of the parameter p and the known ground state binding energy, eq. 16 may be used to

(8) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

(9) D. Steele, E. R. Lippincott, and J. T. Vanderslice, *ibid.*, **34**, 239 (1962).

(10) S. Fraga and R. S. Mulliken, *ibid.*, **32**, 254 (1960).

<div align="center">TABLE I</div>

<div align="center">PARAMETERS USED IN DIATOMIC GROUND[a] AND EXCITED[b] STATE POTENTIALS</div>

Molecule	D_e, e.v.	ω_e, cm.$^{-1}$	$\omega_e x_e$, cm.$^{-1}$	B_e, cm.$^{-1}$	α_e, cm.$^{-1}$	R_e, Å.	a, e.v.	b, bohr^{-1}
$H_2{}^c$	4.75	4400	120.82	60.841	3.018	0.742	10.540	0.8245
HF^c	6.114	4137	88.73	20.946	0.789	0.917	23.330	.9786
HCl^d	4.615	2990	52.05	10.591	.302	1.275	25.906	.8642
HBr^d	3.918	2650	45.21	8.473	.226	1.414	26.857	.8539
HI^d	3.20	2310	39.73	6.551	.183	1.604	24.937	.7951
F_2	1.68^e	892^d	10.97^f	0.631^f	.0073^f	1.435	29.400	1.1867
$Cl_2{}^d$	2.51	565	4.0	.244	.0017	1.988	55.788	0.9204
$Br_2{}^d$	1.99	323	1.07	.081	.0003	2.284	68.118	.9013
$I_2{}^c$	1.56	214	0.61	.037	.0001	2.668	20.791	.5844

[a] Data in col. 2–7 used for Hulburt–Hirschfelder ground state curves.   [b] Parameters a and b appearing in col. 8 and 9 used for excited state curves; see eq. 17.   [c] Ref. 9.   [d] G. Herzberg, "Molecular Structure and Molecular Spectra," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1945.   [e] R. P. Iczkowsky and J. L. Margrave, *J. Chem. Phys.*, **30**, 403 (1959).   [f] Extrapolated from series Cl_2, Br_2, I_2.

estimate the excited triplet state energy for an internuclear distance equal to the ground state *equilibrium* distance. Since the excited triplet state energy is undoubtedly repulsive for all distances, we propose to represent it in general by the simple exponential expression

$$E_2 = ae^{-bR} \qquad (17)$$

Equation 16 may be utilized to determine one of the two constants a and b. For intermediate to large

Results

Calculations were performed for reactions 1–3 using the Hulburt–Hirschfelder ground state potentials and the approximate eq. 17 for the excited triplet state potentials of H_2, X_2, and HX. In determining the excited triplet curves, values of the parameter p ranging from 0.1 to 0.4 were tested. The final results in which $p = 0.15$ is used throughout are displayed as solid curves in Fig. 1–9.
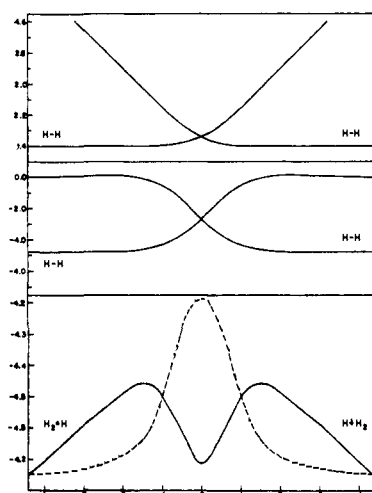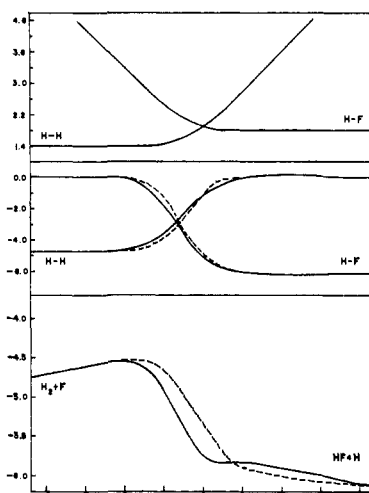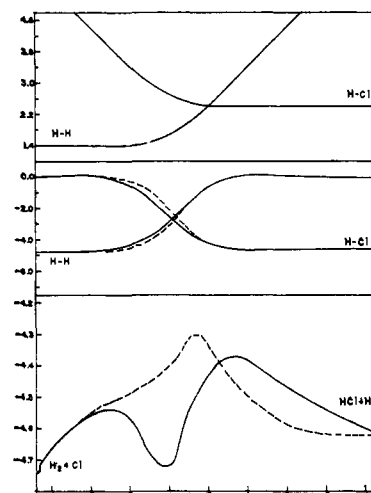

Fig. 1.   Fig. 2.   Fig. 3.

Fig. 1.—Abscissa: reaction coordinate $R_{AB} - R_{BC}$, expressed in bohr units of distance.[12]   Ordinate for lower third: $-\Delta E_{at}$ in e.v. for the linear system ABC, minimized with respect to R_{AB} (or R_{BC}) holding R_{BC} (or R_{AB}) constant; ordinate for middle third: $-B_{AB}$ and $-B_{BC}$ in e.v. (eq. 13); ordinate for upper third: optimum R_{AB} and R_{AC} in bohr units.   Solid lines are results obtained using Hulburt–Hirschfelder ground state diatomic potential energy curves and eq. 17 for excited curves;   dashed lines are results in which accurate ground and excited curves are used for H_2.

Fig. 2.—See caption for Fig. 1;   A = B = H, C = F.

Fig. 3.—See caption for Fig. 1;   A = B = H, C = Cl.

internuclear distances, it has been suggested that the coulomb energy becomes a smaller fraction of the total energy, and that the exchange energy becomes a larger fraction[11]; that is, for larger R, J might be neglected in eq. 15 and $E_1 = -E_2$ (for H_2, this appears to become true at about $R = 4$–5 bohrs[12]). In order to determine the second of the two constants a and b, we let $E_2 = -E_1$ for $R = 4R_e$, except for Br_2 and I_2 (for which R_e is much larger and consequently E_1 was extremely small at $R = 4R_e$), where $R = 3R_e$ was taken. The constants a and b thus obtained are listed in Table I.[13]

(11) F. O. Ellison, *J. Chem. Phys.*, **34**, 2100 (1961).

(12) Internuclear distances are stated throughout this paper in Hartree units; 1 bohr = 0.5292 Å.

(13) This approximation of the excited triplet curve will be quite similar

In the lower third of each figure, the total energy of the system ABC is shown along the optimum reaction coordinate; in the middle third of each figure, the corresponding bond energies B_{AB} and B_{BC} are displayed; and in the top third the optimum internuclear distances R_{AB} and R_{BC} are shown. In Fig. 10, the "nonbonding" interaction energies B_{AC} are graphed for reactions 1 and 2. For all reactions 3, this long-range bond energy is quite small and repulsive, amounting at most to -0.08, -0.06, -0.04, and -0.03 e.v. for X = F, Cl, Br, and I, respectively; it is included in the calculations, of course, and is similar in form to the curves in Fig. 10.

to the "anti-Morse" curve used by Sato[6] and Johnston and Parr[7]: both curves will be identical for $R = R_e$ and both curves will have a simple exponential fall at large distances.
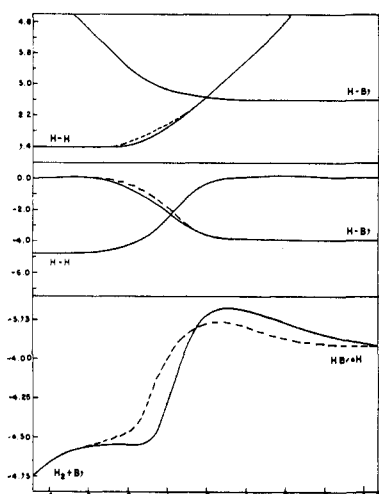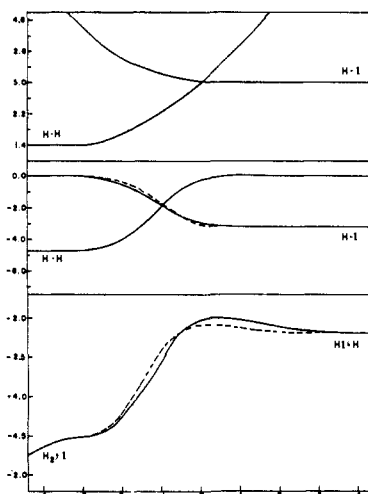
Fig. 4.—See caption for Fig. 1; A = B = H, C = Br.
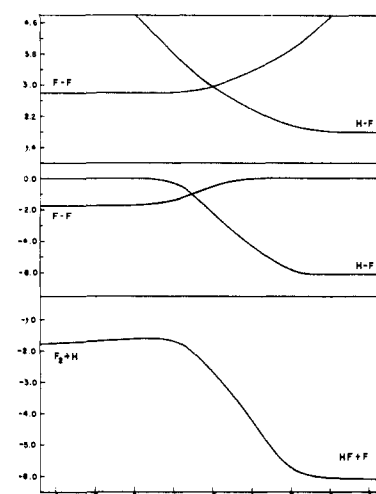

Fig. 5.—See caption for Fig. 1; A = B = H, C = I.
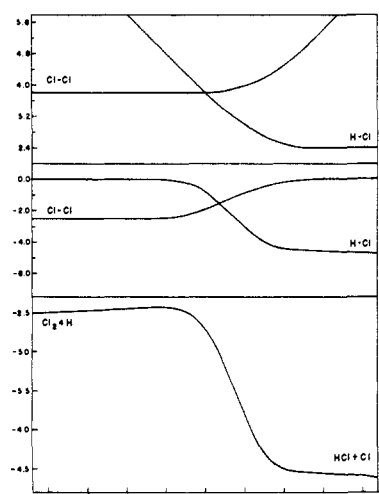

Fig. 6.—See caption for Fig. 1; A = B = F, C = H.
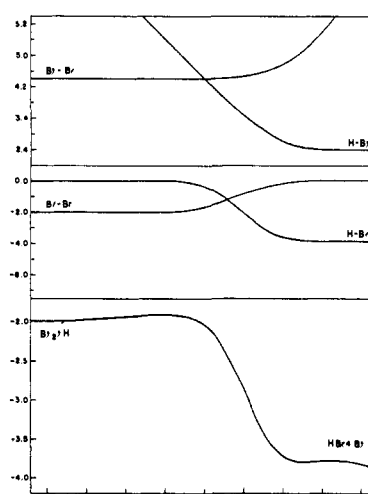

Fig. 7.—See caption for Fig. 1; A = B = Cl, C = H.
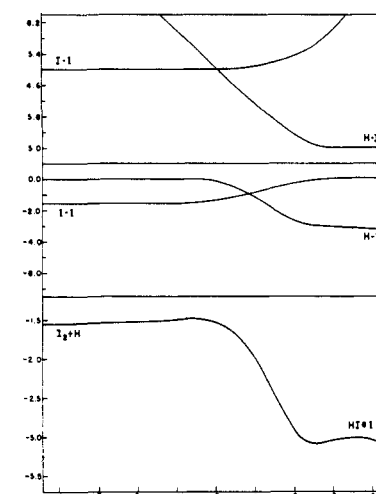

Fig. 8.—See caption for Fig. 1; A = B = Br, C = H.
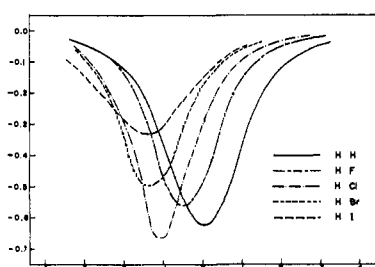

Fig. 9.—See caption for Fig. 1; A = B = I, C = H.

Fig. 10.—B_{HC} bond energy in e.v. (eq. 13), corresponding to "nonbonded interaction between end atoms" in systems HHC, where C = H, F, Cl, Br, or I, plotted against the optimum reaction coordinate $R_{AB} - R_{BC}$ in bohr units.

For reactions 2, calculations were performed also using the same approximate diatomic potential energy curves as above for HX, but *accurate* H_2 ground and excited state potentials were employed. (For reaction 1 involving linear H_3, the more accurate calculations have been reported previously in paper II.) The results are displayed in Fig. 1–5 as dashed curves.

In Table II, classical activation energies calculated for reactions 1–3 according to diatomics in molecules theory are listed and compared with those obtained by Eyring's method, by Sato's method, by the Johnston–Parr method, and by experiment.

Discussion

Aside from the two fundamental assumptions cited in the Introduction, two more necessary approximations are contained in the present work: (1) the use of Hulburt–Hirschfelder ground state potentials; and (2) the use of very simple excited triplet state potentials (eq. 17). Hulburt–Hirschfelder curves are usually very accurate in the region near equilibrium, and thus should not affect adversely the potential energy surfaces near polyatom transition states. However, these approximate potentials do deviate significantly from the truth as R increases. For example, the approximate H_2 ground state curve is essentially correct for $1.2 < R_{HH} < 2.2$; at $R = 3.4$, however, it is 0.14 e.v deeper than the correct one. This is the main cause for the difference between the solid and dashed curves for H_3 (Fig. 1) at $|R_{AB} - R_{BC}| = 2$ and for H_2X (Fig. 2–5) at $R_{HH} - R_{HX} > 1$.

It was found that modification of the parameter p (which determines the diatomic excited triplet curves) in the range 0.1 to 0.4 causes only small (0–2 kcal.) changes in the *classical activation energies* for all of the reactions 1–3. For reactions 3 (Fig. 6–10), changing p only causes the downhill slopes to change in shape. For all other reactions, potential energy "basins" like the

TABLE II

CLASSICAL ACTIVATION ENERGIES (KCAL.)

Reaction	ΔE^a	DIM- ap- prox.^{b}	DIM- acc.^{c}	Expt.^{d}	E.-S.- E.^{e}	Sato^f	J.-P.^{g}
$H_2 + H = H + H_2$	0	6.7	13.0	7.7	7.9	5.4	10
$H_2 + F = H + HF$	−31	5	5	7.5	6.3	0.5	2
$H + HCl = H_2 + Cl$	−3	6	7	4.5	11.4	4.7	5
$H + HBr = H_2 + Br$	−19	6	4	1.2	10.4	0.7	2
$H + HI = H_2 + I$	−35	5	3	1.5	7.7	0.3	1
$F_2 + H = F + FH$	−103	2					
$Cl_2 + H = Cl + ClH$	−49	2		2	2.7		
$Br_2 + H = Br + BrH$	−44	2		1.2	2.1		
$I_2 + H = I + IH$	−38	2		0	1.8		

^{a} ΔE for over-all reaction; zero-point energies not included. Note that the classical activation energy for the reverse reaction may be obtained by subtracting ΔE from the classical activation energy for the forward reaction. ^{b} Present method, using potential energy curves obtained by Hulburt–Hirschfelder formula for ground states and eq. 17 for excited states. ^{c} Present method, using accurate potential energy curves for H_2 but approximate curves for HX. ^{d} First reaction from A. Farkas and L. Farkas, *Proc. Roy. Soc.* (London), **A152**, 124 (1935); all others from list given in ref. 5. ^{e} Ref. 5. ^{f} Ref. 6. ^{g} Ref. 7.

one evident in the H_3 complex were deepened seriously for high values of p; in fact, complexes ABC stable relative to AB + C and to A + BC were sometimes obtained. The cause is obvious: as p is increased, the triplet state energy E_{2e} is lowered according to eq. 16, which leads to an increased resonance energy in the activated complex. For $p = 0.15$, the energy basins disappeared for all reactions 1–3 except for those involving H_3 and H_2Cl; these two cases are exceptional in that reactants and products are either exactly or almost

degenerate ($\Delta E \sim 0$). For H_3, the deep basin can be eliminated almost completely by decreasing the parameter p into the negative range.

Conclusions

Diatomics in molecules theory applied to reactions 1–3 even with the necessary use of approximate diatomic potential curves leads to good predictions for *classical activation energies*. However, the Hulburt–Hirschfelder ground state potentials introduce deviations (up to about 5 kcal.) in the contours when one of the end bonds is significantly longer than its equilibrium length, and our roughly approximated excited state curves cause potential energy depressions or basins (up to about 13 kcal.) when the two end *bond energies* are equal or nearly equal.

Research is now in progress on a new modified atoms-in-molecules model for making fairly rapid and more accurate predictions of diatomic excited (and ground) state potential energy curves.[14] This will make possible applications of diatomics in molecules theory with a minimum set of assumptions; rate constants will also be computed. Even then, it must be recognized that activation energy calculations (and the customary accompanying discussions of existence or nonexistence of potential energy "basins") constitutes the most severe test of any theory of molecular electronic structure; no methods of practical value have yet been developed that yield polyatomic energies more accurate than 5 to 10 kcal.

(14) F. O. Ellison, *J. Chem. Phys.*, to be submitted.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Kinetic Studies of the Catalytic Hydrolysis of 1,3-Dicarboxyphenyl 2-Phosphate and 1-Methoxycarbonyl-3-carboxyphenyl 2-Phosphate[1]

BY YUKITO MURAKAMI[2] AND ARTHUR E. MARTELL[3]

First-order hydrolysis studies of two salicyl phosphate analogs, 1,3-dicarboxyphenyl 2-phosphate (DCPP) and 1-methoxycarbonyl-3-carboxyphenyl 2-phosphate (MCPP), are reported. Maximum rates of spontaneous hydrolysis of DCPP and of MCPP occur at $-\log [H^+] = 3.90$ and 5.50, respectively. The rate constants for hydrolysis of the mono-, di-, and triionic species are evaluated. The 1:1 dipyridyl–Cu(II) chelate system was found to have a strong catalytic effect on the hydrolysis of DCPP in neutral and in alkaline solutions where neither the un-ionized nor the monoionic species is present. The catalytic effect of vanadyl ion on the hydrolysis of MCPP is evaluated from the data obtained in the low pH region. Possible reaction mechanisms involving the formation of cyclic activated complexes are discussed.

This paper describes an extension of the investigation of metal ion and metal chelate catalysis in the hydrolysis of salicyl phosphate reported in preliminary communications.[4] As an approach to the study of the mechanism of catalysis, two analogs of salicyl phosphate, 1,3-dicarboxylphenyl 2-phosphate and 1-methoxycarbonyl-3-carboxyphenyl 2-phosphate were studied

so that the influence of metal ions on these substances might be compared with the effects observed with the parent compound. The work reported up to the present time on monophosphate esters indicates that the un-ionized and the completely ionized phosphate species undergo hydrolysis more slowly than do the intermediate forms. Accordingly, the rate profile has a peak in the middle pH region,[5-11] where the observed

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