A general expression for the dependence of φ_{gas} on the azide concentration is obtained from eq. 10–13.

$$\varphi_{gas} = \Phi + \Phi(1 + 2\alpha + \beta/2)\frac{(N_3^-)}{(N_3^-) + k_3(H_2O)/k_4} \quad (14)$$

The validity of eq. 14 with $k_3(H_2O)/k_4 = 0.2$ is demonstrated in Figure 7. From the intercept of the line we obtain $\Phi = 0.265$ which is nearly identical with that derived from the yields of NH_2OH. The value $1 + 2\alpha + \beta/2 = 1.86$ derived from the slope of the line is 9% higher than that directly calculated, using the values of α and β previously determined.

A Simple, Self-Consistent Electrostatic Model for Quantitative Prediction of the Activation Energies of Four-Center Reactions[1]

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Contribution from Stanford Research Institute, Menlo Park, California. Received April 17, 1965

The Benson–Bose, semi-ion pair model of the transition state for four-center reactions is extended to include the metathesis reactions, $X_2 + Y_2 \rightleftarrows 2XY$, as well as the addition reactions, $X_2 + olefin \rightarrow product$, and $HX + olefin \rightarrow product$. A simple electrostatic model of point dipoles is used which permits direct calculation of the activation energies of these reactions. These calculated values agree with a large number of experimental data to within ±1.3 kcal./mole on the average and a maximum deviation of 3.2 kcal./mole. It was found that the best fit could be obtained by using $r_{X-X} + 0.40$ Å. as the transition-state distance for all X–X bonds, where r_{X-X} is the ground-state X–X distance. The dipole–dipole separation is obtained by adding 1.00 Å. to the r_{X-Y} distance, where X–Y is the bond being formed. This leads to a physically reasonable as well as a self-consistent model. Values are given for about 40 reactions involving X, Y = H, F, Cl, Br, I. A simple point charge correction is included to account for the Markovnikov rule. Attention is directed to the astonishingly low energies required to produce semi-ion pair states in olefins and the consequences for olefin chemistry.

I. Introduction

The polar character of the transition state of four-center reactions is adequately established by experimental evidence.[2,3] This suggests that the activation process can be described quantitatively by an electrostatic analysis. Benson and Bose[3] performed such an analysis for the addition reaction of hydrogen halides to olefins by using for the transition state an intimate association of two semi-ion pairs. In the present article we describe the extension of this semi-ion pair model to the general family of four-center reactions and describe a simple and consistent scheme for predicting the parameters of the transition state.

In dealing with large intramolecular charge separations, the simplest approach is to assume that a molecule can be approximated by a collection of point dipoles and point aggregates of polarizable matter. This avoids the problem of higher-order interactions (quadrupole, octopole, etc.) which are a consequence of the expansion of the electrostatic potential of the charge distribution in terms of a power series. This simple approach is justified if it gives accurate and consistent results.

II. Physical Model

If the metathesis reactions of $AA^* + BB^* \rightarrow A–B + A^*–B^*$ occurs through a four-center cyclic transition state with partial bonds between all atoms, a reasonable electronic development of the process can be shown as in Figure 1.

In order to pass smoothly from the electronic ground state of the reactants (I) (where there are single bonds A–A and B–B but no bonds A–B) to the electronic ground state of the products (V) (where there are single bonds between the AB's and no A–A or B–B bonds), a concerted polarization of the A–A* and the B–B* bonds in opposite directions must occur (II). This state constitutes an association of two semi-ion pairs (the formal charge on the atoms are $1/2$ of the charge of an electron). Energy is required to polarize the single bonds forming the semi-ion pairs. However, part of this electrostatic energy is regained by their mutual interaction in the transition state and it is diminished by the polar energy that might reside in the ground state of the reactants. This charge transfer will continue smoothly through the symmetric state III, with one-electron bonds in all the reaction coordinates. This state is not a transition state in the sense formulated by the transition state theory of chemical reactions. We then find a transition state similiar to II but having the heredity of the products (V). The quantitative equation for predicting the energy of generations of the polar transition state II is

(2) S. W. Benson, *Advan. Photochem.*, 2, 1 (1964).
(3) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, 39, 3463 (1963).

$$E_{\text{calcd}} = \frac{\epsilon^2 \delta^2}{2} \left\{ \frac{r^2_{\text{AA}^*}}{\alpha_{\text{AA}^*}} + \frac{r^2_{\text{BB}^*}}{\alpha_{\text{BB}^*}} - \frac{3}{2} \frac{r_{\text{AA}^*} \cdot r_{\text{BB}^*}}{r_0{}^3} \right\} -$$
$$\frac{\epsilon^2}{2} \left\{ \frac{(\mu^0{}_{\text{AA}^*})^2}{\alpha^0{}_{\text{AA}^*}} + \frac{(\mu^0{}_{\text{BB}^*})^2}{\alpha^0{}_{\text{BB}^*}} \right\} \quad (1)$$

This is for the four-center, exothermic reaction AA* + BB* → AB + A*B* (or else addition to form a single molecule). The distances r_{AA^*}, r_{BB^*}, and r_e are the transition state bond lengths A–A*, B–B*, and the average of the equilibrium distances A–B and A*–B*, respectively. $\alpha^0{}_{\text{AA}^*}$ and $\alpha^0{}_{\text{BB}^*}$ are the longitudinal molar polarizations in the ground state. α_{AA^*} and α_{BB^*} represent a characteristic average for the longitudinal molar polarizations between the ground and the transition states. $\mu^0{}_{\text{AA}^*}$ and $\mu^0{}_{\text{BB}^*}$ are the respective ground-state dipole moments. The quantity δ is equated to the formal charge separation in the transition state II (δ $^1/_2$.) The first and second terms of eq. 1 represent the energies necessary to polarize the reacting bonds of the molecules AA* and BB*. The third term represents the difference in the energy of the dipole–dipole attraction and the intermolecular repulsion assumed to have the form $B/r^{12}{}_e$. The last two terms represent the polarization energy (if any) existing in the ground states of AA* and BB* when thay have permanent dipoles.

The angular dependence of the dipole interaction for any of the geometries involved can be neglected. Although the angular dependence of the dipole–dipole interactions is unimportant, the geometric relationship between the reacting bonds and the distance between the dipole centers (r_e) in a few cases makes a difference of a few kcal./mole. This correction for the distance r_e is estimated by eq. 2. The

$$r_e \simeq \frac{1}{2} \left\{ r_{\text{AB}} \sqrt{1 - \frac{1}{4}\left(\frac{r_{\text{AA}^*} - r_{\text{BB}^*}}{r_{\text{AB}}}\right)^2} + \right.$$
$$\left. r_{\text{A}^*\text{B}^*} \sqrt{1 - \frac{1}{4}\left(\frac{r_{\text{AA}^*} - r_{\text{BB}^*}}{r_{\text{A}^*\text{B}^*}}\right)^2} \right\} \quad (2)$$

secondary polarization effects are not negligible but are small enough to be omitted in this calculation. We have investigated the possible importance of dispersion forces and found that the dispersion energy between ethylene and iodine was less than 0.5 kcal./mole. London's[4] treatment of dispersion forces was used to estimate this interaction energy from the energy of vaporization of the two liquids, the structure of the solvation shell in the liquids, and the ground-state polarizability of the molecules.

The transition state values of the distances and polarizabilities are deduced from ground-state values which are usually known. These deductions will be described in the following sections. In a few cases where data were not available, we have had to make estimates of ground-state values on semiempirical grounds.

III. Estimation of the Parameters of the Transition State

A. Polarizabilities. Equation 1 treats the polarizabilities α_{AA^*} and α_{BB^*} as constants and, because of this, they must represent an average value between the ground-state and the semi-ion pair polarizabilities.

(4) F. London, Z. physik. Chem., B11, 222 (1930); Z. Physik, 60, 491 (1930); Trans. Faraday Soc., 33, 8 (1937).
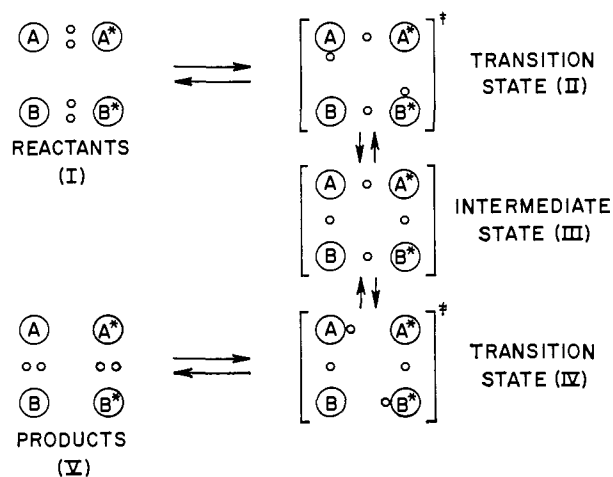
Figure 1. Physical model of a four-center reaction.

This average value was observed to be within 10% of the ground-state polarizabilities for all the molecules in which the polarization for both states could be determined. This fails for the systems involving H_2. This is not surprising when one considers the large change in polarizability that occurs with heterolytic dissociation of the hydrogen molecule into a proton and a hydride ion. The polarizability of the hydride ion appears to be sensitive to the local electrostatic environment. From the index of refractions of crystals[5] it is 10.2 Å.[3] while calculations of the binding energies of gaseous metal hydrides[6] give 1.80 Å.[3]. This difficulty can be circumvented by using the observed energy of activation for the metathesis reaction between H_2 and I_2 to fix the transition state polarizability of hydrogen. The value ($\alpha_{\text{HH}} = 1.40$ Å.[3]) arrived at in this way is nearly the average of the two extremes: the ground-state value ($\alpha_{\text{HH}} = 0.93$ Å.[3]) and the hydride ion value ($\alpha_{\text{H}^-} = 1.80$ Å.[3]).

B. Bond Distances. The leading terms in eq. 1 depend on the square of the interatomic distances and so will be quite sensitive to the proper choice of distances. Fortunately, the range of physically reasonable values for the interatomic distances is narrow so that the model is not quite so flexible as a first glance at eq. 1 might suggest. We shall now consider this in detail.

1. Carbon–Carbon Bond Length. In the addition reaction with olefins the carbon–carbon will approach the equivalent of a three-electron bond (see excited state III). Consequently, we have used the carbon–carbon distance in benzene as a reasonable value for this distance in the transition state.

2. A–A* and B–B* Bond Lengths. The assignment of bond distances by Benson and Bose[3] was based on the assumption that the semi-ion pair will be half-way between the ground-state distance and the complete ion-pair distance. The unknown ionic radii of atoms were guessed from calculations by the screening constants method[7] and/or by isoelectronic considerations. Although this choice of interatomic distance for the

(5) K. Fajans and G. Joos, Z. Physik, 23, 1 (1924).
(6) W. A. Klamperer and J. L. Margrave, J. Chem. Phys., 19, 527 (1951).
(7) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 951.

I —→ (0.43) —→ O

1.14 Å

O —→ (0.12) —→ I   O —→ (0.12) —→ I

2.61 Å   2.42 Å   2.61 Å

I - - - - I

3.07 Å

I —→ (0.43) —→ O

2 —→ (1.5) —→ I

1.40 Å

C = = = C

2.09 Å   2.60 Å   3.13 Å

O —→ (0.12) —→ I   O —→ (0.12) —→ I
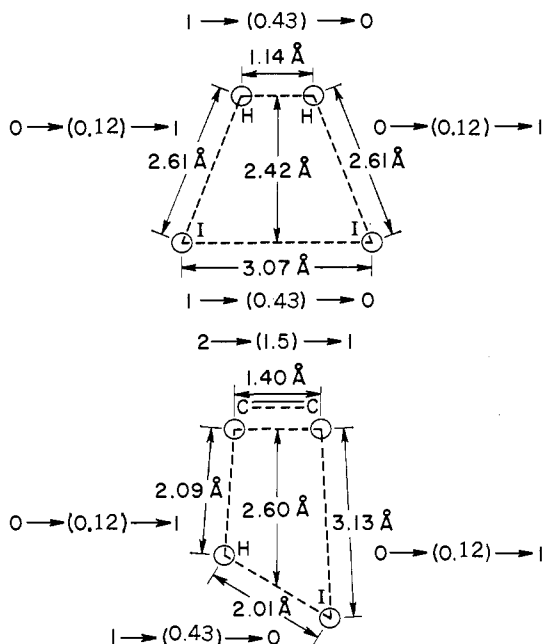
2.01 Å

I —→ (0.43) —→ O

Figure 2. Pictorial representation of typical four-center transition states. The values in parentheses correspond to transition state II. The numbers on the left of the arrows refer to the reactants; those on the right refer to the products.

reaction coordinates A–A* and B–B* permits agreement between calculated and observed energies of activation by adjustment of the dipole–dipole distance denoted by r_e, the application of this rule to several types of four-center reactions does not allow a physically reasonable prescription for establishing the quantity r_e.

We attempted to improve this method by investigating the simple hypothesis that the interatomic distances r_{AA*} and r_{BB*} were linear functions of the ionic character of the bond. The transition-state distance for these reaction coordinates was equated to a semi-ionic bond length; this distance had to be rectified for the ionic character that existed in the ground state so that uniformity could be retained. Although this gave as good agreement as the original method, it still left the same small inconsistencies in the r_e values.

A careful consideration of all of the different values of the transition-state distances arrived at by these two assignments indicated that a much simpler method, leading to equally good predictions of activation energy could be arrived at by adding 0.40 Å. to the ground-state values of r_{AA*} and r_{BB*}. We shall consider this result in more detail later on.

3. Dipole–Dipole Distance r_e. Evaluation of the dipole–dipole distance r_e (distance separating the centers of the dipoles formed by the two semi-ion pairs) was developed generally along the same lines as described above for the A–A* and B–B* bond lengths. The averaging of the single ground-state bond length and the ionic bond length gave good results for activation energy but never quite free of inconsistencies.

The assumption that the r_{AB} and r_{A*B*} values lie half-way between the ground-state single bond length and the van der Waals bond length gave values of r_e which produced surprisingly improved predictions. However, close scrutiny of these values showed that they were very close to values obtained by adding a

constant 0.80 Å. to the ground-state single bond lengths. Trial and error soon revealed that an excellent fit to all data could be obtained by using 1.0 Å. for this constant. At this point some remarks about the relationship between the A–B and A*–B* bond lengths and the distance between the dipole centers, r_e, are appropriate. In the case when the reactants A–A* and B–B* are homonuclear, the distance r_e is precisely a projection of the enlarged A–B bond length on the line of centers (eq. 2). This projection is very nearly equal to the expanded A–B bond length for most of the systems. The case for the heteronuclear reactants is different; the distance r_e is an average of the projection of the A–B and A*–B* expanded bond lengths onto the line of centers (eq. 2). Again the difference in the average of the A–B and A*–B* enlarged bond lengths and the average of their projection is small for nearly all of the systems studied.

4. Bond Character of the Transition State. The discovery that an excellent fit to the data could be obtained by assuming that all single bonds being broken were enlarged by a constant (0.40 Å.) in the transition state, while all single bonds being formed were enlarged by another constant amount (1.0 Å.) over their final values is at first sight very surprising. However, these findings seem much more reasonable when viewed in the light of empirical correlations between bond lengths and bond order.

Johnston and Parr[3] have empirically shown that a reasonable approximation to a zero-order bond is represented by a van der Waals interaction. Application of this concept to the correlation of bond order and bond length[9] results in a relationship for fractional bonds between single and zero order; $D_n = D_1 = [(D_{n_0} - D_1)/\log n_0] \log n$, where D_n represents the bond length for order n (i.e., D_1, single bond length, and D_{n_0}, van der Waals bond length), and n represents bond order (n_0 is the very small bond order associated with a van der Waals bond). The bond order, n_0, is required to be a constant, independent of the system under consideration. The justification of this condition is indicated by the constancy of the quantity, $D_{n_0} - D_1$. An estimate of the bond orders in transition state II can be made if the value of the constant $(D_{n_0} - D_1)/$

Table I. Comparison of Forward and Reverse Transition State Energetics

| Reaction | ΔE° (0°K.),[a] kcal./mole | — E_{calcd} (0°K.), — kcal./mole | | Difference in the energy of transition states II and IV, kcal./mole[c] |
		Forward reaction[b]	Reverse reaction[b]	
$H_2 + I_2 \rightleftarrows 2HI$	−2.18	45.6	38.0	−9.8
$H_2 + Br_2 \rightleftarrows 2HBr$	−16.8	53.6	49.2	−21.2
$H_2 + Cl_2 \rightleftarrows 2HCl$	−44.0	58.2	55.6	−46.6
$H_2 + F_2 \rightleftarrows 2HF$	−128.2	100.8	88.3	−141
$H_2 + H_2* \rightleftarrows 2HH*$	0.00	61.5	61.5	0.00

[a] These values were derived from the heat of formation reported in National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950. [b] See Table V. [c] This quantity is the heat released at 0°K. in going from transition state II to transition state IV at constant volume.

(8) H. S. Johnston and C. Parr, J. Am. Chem. Soc., 85, 2544 (1963).
(9) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

Table II. Parameters used in the Calculation of the Energy of Formation of the Transition State

Bond	αAA* or αBB*	r^{0b}	μ^{0c}	Bonds formed[e] Bonds	r^{0b}
H–I	6.58	1.6I	0.382	C–H	1.09
H–Br	4.23	1.41	0.788	C–I	2.13
H–Cl	3.13	1.27	1.07	C–Br	1.94
H–F	0.96	0.918	1.83	C–Cl	1.77
				C–F	1.38
I–I	17.3	2.67	0.00		
Br–Br	9.60	2.28	0.00	H–I	1.61
Cl–Cl	6.60	1.99	0.00	H–Br	1.41
F–F	1.69	1.42	0.00	H–Cl	1.27
H–H	1.40	0.742	0.00	H–F	0.918
Cl–F	3.1	1.63	0.881	H–H	0.742
Cl–Br	9.0	2.14	0.57	I–I	2.67
Cl–I	11.9	2.32	0.65	Br–Br	2.28
Br–F	4.4	1.76	1.29	Cl–Cl	1.99
Br–I	14.0	2.50	1.21	F–F	1.42
CH2=CH2'	5.61	1.34	0.00	Br–I	2.50
CH3CH=CH2'	8.22	1.34	0.00	Cl–I	2.32
(CH3)2C=CH2'	10.9	1.34	0.00	Cl–Br	2.14
CH3CH=CHCH3'	10.9	1.34	0.00	Br–F	1.76
				Cl–F	1.63
CH=CHCH=CHCH2'	10.9	1.35	0.00		
CH3CH2CH=CH2'	9.02	1.34	0.00		
CH=CHCH=CHCH2CH2'	10.9	1.35	0.00		

[a] In all cases, except HH, $\alpha_{AA}*$ or $\alpha_{BB}*$ represents the ground-state longitudinal polarizability of the bond or molecule. The longitudinal polarizability of H_2 bond is an average of the ground-state and excited state polarizabilities; see text for details. Ground-state polarizabilities were obtained from the following references: (a) S.-N. Wang, *J. Chem. Phys.*, **7**, 1012 (1939); (b) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940); (c) C. H. Douglas Clark, *Nature*, **153**, 585 (1934); (d) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Dover Publications, New York, N. Y., 1964; (e) J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1964; (f) Landolt-Börnstein, "Zahlenwertie and Funktionen," Vol. I, "Atom und Molecular Physik," Part 3, "Molekeln II." The axes of the ellipsoid of polarization of many molecules have been determined (footnotes a, b, and f). The unknown ratio of transverse to longitudinal polarizabilities were assumed to have the same value as that of a chemically similar molecule for which this ratio was known. The longitudinal polarizabilities of the interhalogens have been estimated by extrapolation between the known values of the halogens using an empirical extrapolation function described by Denbigh (b). The longitudinal polarizability of cyclopentadiene was assumed to be the same as that measured for butene-2. [b] Ground-state, bond lengths were obtained from L. E. Sutton, "Table of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958. [c] Dipole moments of the reactants were obtained from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. [d] Transition-state bond lengths, $r^0 + 0.40$ Å. The double bonds in the olefins are assumed to be 3-electron bond in the transition state. We have equated this transition state bond length with the carbon–carbon distance in benzene (1.40 Å.). [e] Transition-state bond lengths, $r^0 + 1.0$ Å. [f] The following abbreviated notation will be used in the remaining tables: $CH_2=CH_2$, C_2H_4; $CH_3CH=CH_2$, C_3H_6; $(CH_3)_2C=CH_2$, *i*-C_4H_8; $CH_3CH=CHCH_3$, *s*-C_4H_8; $\overline{CH=CHCH=CHCH_2}$, C_5H_6; $CH_3CH_2CH=CH_2$, *n*-C_4H_8; $\overline{CH=CHCH=CHCH_2CH_2}$, C_6H_8.
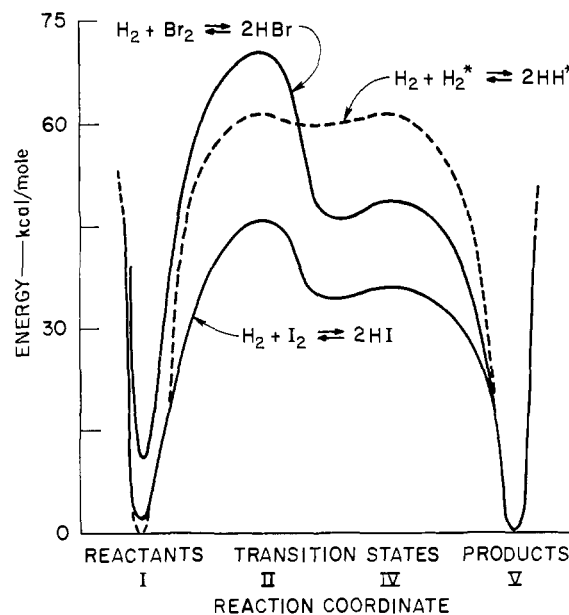

Figure 3. Energy diagram for the activation process.

$(D_{n_0} - D_1)/\log n_0 \approx 1.1$. Consequently, a bond enlargement of 0.40 and 1.0 Å. corresponds to a bond order of 0.43 and 0.12, respectively. The pictorial representations of the transition state II implies a $1/2$-order bond in the bond-breaking coordinates and weaker bonding in the bond-forming coordinates. Accordingly, the constant bond enlargement for all the systems corresponds to a constant bond character for the transition state II, and the unsymmetrical bond enlargement for the different reaction coordinates corresponds to the asymmetry of the bond order of these coordinates in the transition state II.

5. Asymmetry of the Transition State. The nonequivalence of the bond character of the rupturing and evolving bonds attributes an asymmetry to the transition state, *i.e.*, the character of the transition state is nearer that of the reactants than the products. This asymmetry disappears for the systems that have zero heat of reactions, in view of the fact that the energies of the transition states II and IV are the same. As the exothermicity of the reaction increases, the energy content of the transition state IV becomes less than that of the transition state II (see Table I). Consequently, the potential energy curve for the transition state of a reaction with zero heat of reaction is a broad, flat hump, possibly even with a shallow minimum in it. With increasing exothermocity the reaction develops a peak which is skewed toward the higher energy reactants (see Figure 3). This quantitative description of the transition state concurs with the generalization proposed by Hammond,[10] "in highly exothermic steps it will be expected that the transition states will resemble reactants closely and in endothermic steps the products will provide the best models for the transitions states."

IV. Comparison of the Predicted and Observed Activation Energies

The complete details of the calculation of activation energies are given in Tables II to VII. The electro-

(10) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

log n_0 is determined. An examination of the bond order and bond length for different types of hydrogen atom interactions (H_2, $n = 1$ and $D_1 = 0.74$ Å.; H_2^+, $n = 1/2$ and $D_{1/2} = 1.06$ Å. (known $1/2$ order bond); $H \cdots H$ (van der Waals interactions), $n \sim 0$ and $D_{n_0} = 2.4$ Å.) allows an estimate of this constant,

Table III. Activation Energies for the Addition of HX to Olefins to Form RX[a]

Reaction AA* + BB* → products	E_{AA*}[b]	E_{BB*}[c]	E_{int}[d]	E_{gs}[e]	E_{total}[f] (0°K.)	E_{act}^{calcd}[g] (298°K.)	E_{act}^{obsd}[h] (298°K)	Δ[i]
a-1								
HI + C_2H_4	25.5	14.5	10.0	0.16	29.8	29.0	28.4	+0.6
+ C_3H_6[k]		9.90			25.2	24.4	23.7	+0.7
+ C_3H_6 [l]		9.90			25.2	29.4		
+ i-C_4H_8[k]		7.46			22.8	17.0	18.2	−1.2
+ i-C_4H_8[l]		7.46			22.8	27.0		
+ s-C_4H_8		7.46			22.8	22.0	21.3	+0.5
+ n-C_4H_8[k]		9.03			24.3	23.5		
+ n-C_4H_8[l]		9.03			24.3	28.5		
a-2								
HBr + C_2H_4	32.2	14.5	10.1	1.06	35.5	34.7	34.4	+0.3
+ C_3H_6[k]		9.90			30.9	30.1	28.3	+1.8
+ C_3H_6[l]		9.90			30.9	35.1	34.2	+0.9
+ i-C_4H_8[k]		7.46			28.5	22.7	23.3	−0.6
+ i-C_4H_8[l]		7.46			28.5	32.7		
+ s-C_4H_8		7.46			28.5	27.7	27.9	−0.2
+ n-C_4H_8[k]		9.03			30.0	29.2	26.9	+2.3
+ n-C_4H_8[l]		9.03			30.0	34.2	33.6	+0.6
a-3								
HCl + C_2H_4	37.0	14.5	10.2	2.63	38.7	37.9	40.6	−2.7
+ C_3H_6[k]		9.90			34.1	33.3	32.6	+0.7
+ C_3H_6[l]		9.90			34.1	38.3	40.0	−1.7
+ i-C_4H_8[k]		7.46			31.7	25.9	25.8	+0.1
+ i-C_4H_8[l]		7.46			31.7	35.9		
+ s-C_4H_8		7.46			31.7	30.9	33.2	−2.3
+ n-C_4H_8[k]		9.03			33.2	32.4	32.2	+0.2
+ n-C_4H_8[l]		9.03			33.2	37.4	39.8	−2.4
a-4								
HF + C_2H_4	75.4	14.5	10.3	25.2	54.4	53.8	54 ± 3[j]	−0.2
+ C_3H_6[k]		9.90			49.8	49.0		
+ C_3H_6[l]		9.90			49.8	54.0		
+ i-C_4H_8[k]		7.46			47.4	41.6		
+ i-C_4H_8		7.46			47.4	51.6		
+ s-C_4H_8		7.46			47.4	46.6		
+ n-C_4H_8[k]		9.03			48.9	48.9		
+ n-C_4H_8[l]		9.03			48.9	53.9		

[a] r_e, the distance between the dipole centers (the projection of the average of the bond lengths AB and A*B* onto the line of centers as estimated by eq. 2), is (Å.): *a-1*, 2.60; *a-2*, 2.51; *a-3*, 2.43; *a-4*, 2.24. [b] $E_{AA*} = (\epsilon^2/8)(r^2_{AA*}/\alpha_{AA*})$, where the values of r_{AA*} and α_{AA*} are tabulated in Table II (kcal./mole). [c] $E_{BB*} = (\epsilon^3/8)(r^2_{BB*}/\alpha_{BB*})$, where the values of r_{BB*} and α_{BB*} are tabulated in Table II (kcal./mole). [d] $E_{int} = (3/2)(\epsilon^2/8)(r_{AA*}r_{BB*}/r_e^3)$. This term represents the dipole–dipole interaction and the repulsive energy in the transition state (kcal./mole). [e] $E_{gs} = (\epsilon^2/2)(\mu^2_{AA*}/\alpha^{\circ\prime\prime}_{AA*})$, where μ_{AA*} represents the ground-state dipole moment of AA* and $\alpha^{\circ\prime\prime}_{AA*}$ represents the longitudinal ground state polarizability of AA*; both of these quantities are tabulated in Table II. This term represents the polarization energy of AA* in the ground state (kcal./mole). [f] E_{total} (0°K.) = $E_{AA*} + E_{BB*} − E_{int} − E_{gs}$ (kcal./mole). [g] E_{act} (298°K.) represents the calculated activation energy at 298°K. E_{act} (298°K.) = E_{total} (0°K.) + $E_{thermal}$ + $E_{point charge}$, where $E_{thermal}$ represent the change in the activation energy on heating the system from 0 to 298°K. and $E_{point charge}$ represents the correction in the activation energy due to point charge effects; see text for details. $E_{thermal}$ is −0.8 kcal./mole for all the reactions tabulated in this table; $E_{point charge}$, see footnotes k and l. [h] E_{act} (298°K.) represents the observed activation energy at 298°K.; see Table VII. [i] Δ indicates the deviation between observed and calculated activation energies; $\Delta = E_{act}^{calcd} − E_{act}^{obsd}$. [j] Estimated from the disproportionation/combination ratio for CFH₂ radicals (S. W. Benson and G. R. Haugen, to be published). [k] "Markovnikov" addition; $E_{point charge}$ is zero, except for i-C_4H_8 where it is −5.0 kcal./mole. [l] Anti-Markovnikov addition $E_{point charge}$ is +0.5 kcal./mole.

static calculation neglects the change in thermal energy content of the reactants upon activation, and for this reason the calculated activation energies refer to absolute zero. Comparison of the observed and predicted activation energies demands the adjustment of the calculated and observed values from the experimental temperature to some common temperature which we have chosen as 298°K. These adjustments are contingent on estimating heat capacity of the transition states. The corrections are never larger than 2 kcal./mole and the error in them was estimated to be less than the experimental error in the activation energies.

The consequence of the substitution of the point charge distribution in the transition state by the point dipole approximation is apparent in the nonpredictability of the directive effect (Markovnikov rule[11])

(11) W. Markovnikov, *Ann.*, **153**, 256 (1870).

of the attached methyl groups. Benson and Bose[8] correlate this effect with the difference in the geometrical distribution of the positive and negative charges. Only a model which treats the transition state as a microscopic point charge distribution can be expected to correlate completely the methyl effects. In the simple dipole model the methyl effect is attributed to the effect of changing H to CH_3 on the macroscopic homogeneous polarizability of the olefins. This model predicts the same activation energy for isobutene and butene-2, since the longitudinal macroscopic polarizability of the olefins is not sensitive to the arrangement of the methyl groups around the double bond. On the other hand, the effect of the distribution of the polarizable matter on the polarization energy of a positive point charge is demonstrated[3] by the 21-kcal./mole difference in the energies of formation of the *n*-propyl and isopropyl ions: I.P.(n-C_3H_7) − I.P.(i-C_3H_7)

Table IV. Activation Energies for Molecular Exchange Reactions[a]

Reaction AA* + BB* → products		r_s, Å[b]	E_{AA^*}[c]	E_{BB^*}[d]	E_{int}[e]	E_{gs}[f]	E_{total} (0°K.)[g]	$E_{thermal}$[h]	E_{act}^{calcd} (298°K.)[h]	E_{act}^{obsd} (298°K.)[i]
a-1										
I₂	+ H₂	2.42	22.6	38.5	15.5	0.00	45.6	−1.1	44.5	41.6
Br₂	+ H₂	2.29	31.0		15.9		53.6	−1.1	52.5	≥31[i]
Cl₂	+ H₂	2.18	36.0		16.3		58.2	−0.9	57.3	≥26[i]
F₂	+ H₂	1.89	81.5		19.2		100.8	−0.9	99.9	≥45[i,k]
H₂*	+ H₂[l]	1.74	38.5		15.5		61.5	−0.8	60.7	
a-2										
H*I*	+ HI[l]	2.61	25.5	25.5	14.3	0.32[n]	36.4	−0.8	35.6	
H*Br*	+ HBr[l]	2.41	32.2	32.2	14.6	2.12[n]	47.7	−0.8	46.9	
H*Cl*	+ HCl	2.27	37.0	37.0	15.0	5.26[n]	53.7	−0.8	52.9	
H*F*	+ HF	1.92	75.4	75.4	15.5	50.4[n]	84.9	−0.8	84.1	
a-3										
HI	+ HI	2.71	25.5	25.5	12.7	0.32[n]	38.0[m]			
HBr	+ HBr	2.51	32.2	32.2	13.1	2.12[n]	49.2[m]			
HCl	+ HCl	2.37	37.0	37.0	13.1	5.26[n]	55.6[m]			
HF	+ HF	2.08	75.4	75.4	12.1	50.4[n]	88.3[m]			
HH*	+ HH*[l]	1.74	38.5	38.5	15.5	0.00	61.5[m]			
a-4										
H*I	+ H₂[l]	2.14	25.5	38.5	14.6	0.16	49.2	−0.8	48.4	
H*Br	+ H₂[l]	2.05	32.2		14.9	1.06	54.7	−0.8	53.9	≥42[i]
H*Cl	+ H₂[l]	2.00	37.0		14.8	2.63	58.1	−0.8	57.3	≥43[i]
H*F	+ H₂[l]	1.83	75.4		15.4	25.2	73.3	−0.8	72.5	
a-5										
HI*	+ I₂[l]	3.10	25.5	22.6	13.0	0.16	34.9	−1.1	33.8	
HBr*	+ Br₂[l]	2.82	32.2	31.0	13.5	1.06	48.6	−1.1	47.5	≥19[i]
HCl*	+ Cl₂[l]	2.62	37.0	36.0	13.9	2.63	56.5	−0.9	55.6	≥25[i]
HF*	+ F₂[l]	2.17	75.4	81.5	14.7	25.2	117.0	−0.9	116.1	
a-6										
Cl₂	+ F₂	2.62	36.0	81.5	15.1	0.00	102.4	−1.1	101.3	
Cl₂	+ Br₂	3.14		31.0	12.9		54.1	−1.2	52.9	
Cl₂	+ I₂	3.31		22.6	12.7		45.9	−1.2	44.7	
Br₂	+ F₂	2.73	31.0	81.5	15.0		97.5	−1.2	96.3	
Br₂	+ I₂	3.50		22.6	12.0		41.6	−1.4	40.2	
a-7										
ClF	+ H₂	2.05	55.3	38.5	16.8	1.78	75.2	−0.9	74.3	
ClBr	+ H₂	2.24	29.8		16.1	0.23	52.0	−1.0	51.0	
ClI	+ H₂	2.31	25.8		15.7	0.26	48.3	−1.0	47.3	
BrF	+ H₂	2.11	44.0		16.3	2.70	63.5	−1.0	62.5	
BrI	+ H₂	2.36	25.0		15.7	0.75	47.0	−1.1	45.9	
a-8										
HI	+ ClI	2.95	25.5	25.8	13.3	0.42[n]	37.6	−1.0	36.5	
HI	+ BrI	3.02			13.2	0.91[n]	36.4	−1.0	35.4	
HBr	+ ClBr	2.75	32.2	29.8	13.9	1.29[n]	46.8	−1.0	45.8	
HCl	+ FCl	2.46	37.0	55.3	14.3	4.41[n]	73.6	−0.9	72.7	
HBr	+ FBr	2.60	32.2	44.0	13.9	3.76[n]	58.5	−1.0	57.5	
a-9										
HI	+ Br₂	2.94	25.5	31.0	13.2	0.16	43.1	−1.1	42.0	
HI	+ Cl₂	2.80		36.0	13.7		47.6	−0.9	46.7	
HBr	+ Cl₂	2.70	32.2		13.8	1.06	53.3	−0.9	52.4	
HBr	+ F₂	2.34		81.5	16.2		96.4	−0.9	95.5	
HCl	+ F₂	2.28	37.0		16.0	2.63	99.9	−0.9	99.0	

[a] The type of exchange reactions are denoted as follows: a-1 and a-6, $x^2 + y^2 \rightarrow 2xy$; a-2, $xy + wz \rightarrow xz + yw$; a-3, $2xy \rightarrow x_2 + y_2$; a-4, a-5, a-7, and a-9, $xy + z^2 \rightarrow zy + xz$; a-8, $xy + zy \rightarrow xz + y^2$. [b] r_e represents the distance between the dipole centers. It is the projection of the average of the bond lengths AB and A*B* onto the line of centers as estimated by eq. 2. [c] See footnote b, Table III. [d] See footnote c, Table III. [e] See footnote d, Table III. [f] See footnote e, Table III. [g] See footnote f, Table III. [h] See footnote g, Table III. [i] See footnote h, Table III. [j] Lower limit for the activation energy of molecular exchange estimated from the measured rate of radical exchange. [k] The lower limit for the activation energy of ortho–para H_2 exchange is 45 kcal./mole and the lower limit for H_2–D_2 exchange is 47 kcal./mole. [l] Asterisk represents labeling that makes the two species distinguishable but chemically equivalent; for example: H_2^* represents D_2, o-H_2, or p-H_2. [m] This is only part of the activation energy for these reactions since their endothermic; see Table I. [n] This represents the sum of the ground-state polarization energy of both reactants.

~ 0.9 e.v. This difference in polarization energy would be about 5 kcal./mole if one-half of an electronic charge is situated on the carbon atom. On account of this, the asymmetry of the polarizable matter in isobutene was taken into account by reducing the calculated activation energies by 5 kcal./mole. There is a 5-kcal./mole increase in the activation energy for every methyl group that does not contribute to the stabilization of the positive charge. The relationship of the structure of the four-center transition state to the application of this correction is indicated in Tables II–VII.

In some cases a lower limit to the activation energy for the four-center addition or exchange reaction has been indicated. These were deduced from the experimental observed rates (mechanism generally was radical chain) by assuming that 10% or less of the rate corresponded to a four-center mechanism. The addi-

Table V. Activation Energies for the Addition of X_2 to Olefins to Form RX_2[a]

Reaction AA* + BB* → products	E_{AA*}[b]	E_{BB*}[c]	E_{int}[d]	E_{total}[e] (0°K.)	E_{act}^{calcd}[f] (298°K.)	E_{act}^{obsd}[g] (298°K.)	Δ[h]
a-1							
I_2 + C_2H_4	22.6	14.5	9.74	27.4	26.2	26.1	+0.1
+ C_3H_6		9.90		22.8	21.6		
+ i-C_4H_8		7.46		20.4	14.2		
+ s-C_4H_8		7.46		20.4	19.2		
a-2							
Br_2 + C_2H_4	31.0	14.5	9.84	35.7	34.5		
+ C_3H_6		9.90		31.1	29.9		
+ i-C_4H_8		7.46		28.7	22.5		
+ s-C_4H_8		7.46		28.7	27.5		
a-3							
Cl_2 + C_2H_4	36.0	14.5	10.3	40.2	39.3		
+ C_3H_6		9.90		35.6	34.7		
+ i-C_4H_8		7.46		33.2	27.3		
+ s-C_4H_8		7.46		33.2	32.3		
a-4							
F_2 + C_2H_4	81.5	14.5	11.8	84.2	83.3		
+ C_3H_6		9.90		79.6	78.7		
+ i-C_4H_8		7.46		77.2	71.3		
+ s-C_4H_8		7.46		77.2	76.3		
a-5							
H_2 + C_2H_4	38.5	14.5	10.9	42.1	41.3	$\geq$38[i]	
+ C_3H_6		9.90		37.5	36.7	$\geq$38[i]	
+ i-C_4H_8		7.46		35.1	29.3	$\geq$37[i]	
+ s-C_4H_8		7.46		35.1	34.3		
+ C_5H_6		7.46[i]		35.1	34.5	35.8	-1.3
+ C_6H_8		7.46[i]		35.1	34.5	35.8	-1.3

[a] r_e, the distance between the dipole centers (the projection of the average of the bond lengths AB and A*B* onto the line of centers as estimated by eq. 2) is (Å.): a-1, 3.02; a-2, 2.88; a-3, 2.73; α-4, 2.38; a-5, 2.09. [b] See footnote b, Table III. [c] See footnote c, Table III. [d] See footnote d, Table III. [e] See footnote f, Table III. E_{ge} is zero for all the reactions tabulated in this table. [f] See footnote g, Table III. $E_{thermal}$ is (kcal./mole): a-1 and a-2, −1.2; a-3 and a-4, −0.9; a-5, −0.8. $E_{point\ charge}$ is zero, except for i-C_4H_8 where it is −5.0 kcal./mole. [g] See footnote h, Table III. [h] See footnote i, Table III. [i] Assumed that the polarizabilities, α_{BB*}, of C_5H_6 and C_6H_8 are the same as the longitudinal polarizability of butene-2. [j] Lower limit for the activation energy of molecular addition estimated from the measured rate of pyrolysis.

Table VI. Activation Energies for the Addition of XY to Olefins to Form RXY[a]

Reaction AA* + BB* → products	E_{AA*}[b]	E_{BB*}[c]	E_{int}[d]	E_{ge}[e]	E_{total}[f] (0°K.)	$E_{thermal}$[g]	E_{act}^{calcd}[g] (298°K.)
a-1							
ClF + C_2H_4	55.3	14.5	10.7	1.78	57.3	-0.9	56.4
+ C_3H_6		9.90			52.7	-0.9	51.8
+ i-C_4H_8		7.46			50.3	-0.9	44.4
+ s-C_4H_8		7.46			50.3	-0.9	49.4
a-2							
ClI + C_2H_4	25.8	14.5	9.87	0.26	30.1	-1.1	29.0
+ C_3H_6		9.90			25.5	-1.1	24.4
+ i-C_4H_8		7.46			23.1	-1.1	17.0
+ s-C_4H_8		7.46			23.1	-0.9	22.2
a-3							
BrF + C_2H_4	44.0	14.5	10.2	2.70	45.6	-0.9	44.7
+ C_3H_6		9.90			41.0	-0.9	40.1
+ i-C_4H_8		7.46			38.6	-1.1	32.7
+ s-C_4H_8		7.46			38.6	-0.9	37.7
a-4							
ClBr + C_2H_4	29.8	14.5	10.1	0.23	34.0	-1.1	32.9
+ C_3H_6		9.90			29.4	-1.1	28.3
+ i-C_4H_8		7.46			27.0	-1.1	20.9
+ s-C_4H_8		7.46			27.0	-0.9	26.1
a-5							
BrI + C_2H_4	25.0	14.5	9.91	0.75	28.8	-1.2	27.6
+ C_3H_6		9.90			24.2	-1.2	23.0
+ i-C_4H_8		7.46			21.8	-1.2	15.6
+ s-C_4H_8		7.46			21.8	-0.9	20.9

[a] r_e, the distance between the dipole centers (the projection of the average of the bond lengths AB and A*B* onto the line of centers as estimated by eq. 2) is (Å.): a-1, 2.56; a-2, 2.89; a-3, 2.64; a-4, 2.81; a-5, 2.95. [b-f] See footnotes b through f, Table III. [g] See footnote g, Table III. $E_{point\ charge}$ is zero, except for i-C_4H_8 where it is −5.0 kcal./mole.

tion of hydrogen to isobutene is the only case where the predicted activation energy is smaller than the lower limit. This implies that considerable four-center dehydrogenation may occur in the pyrolysis of isobutane, whereas it is negligible in the ethane and propane pyrolysis.

Table VII. Observed Activation Energies

Reaction	T_m, °K[a]	Log A[b]	E_{T_m}[c]	$E_{(298°K)}$[d]	$\Delta E°_{(298°K)}$[e]	Reverse reaction $E_{(298°K)}$[f]	Ref.
$HI + CH_2=CH_2 \rightarrow CH_2ICH_3$	580	8.48	28.5	28.4			l
$HI + CH_3CH=CH_2 \rightarrow CH_3CHICH_3$	590	7.89	23.5	23.7			l
$HI + (CH_3)_2C=CH_2 \rightarrow (CH_3)_2CICH_3$	500	6.57	18.1	18.2			l
$HI + CH_3CH=CHCH_3 \rightarrow CH_3CHICH_2CH_3$	590	6.26	21.1	21.3			m
$CH_3CH_2Br \rightarrow CH_2=CH_2 + HBr$	720	13.44	53.9	53.9	19.5	34.4	l
$CH_3CHBrCH_3 \rightarrow CH_3CH=CH_2 + HBr$	700	12.7	47.0	47.4	19.1	28.3	l
$CH_3CH_2CH_2Br \rightarrow CH_3CH=CH_2 + HBr$	640	12.9	50.7	51.0	16.8	34.2	l
$(CH_3)_2CBrCH_3 \rightarrow (CH_3)_2C=CH_2 + HBr$	560	12.6[i]	39.0[i]	39.5	16.2	23.3	l
$CH_3CHBrCH_2CH_3 \rightarrow CH_3CH=CHCH_3 + HBr$	600	12.7[i]	44.6[i,k]	44.8	16.9	27.9	l
$CH_3CHBrCH_2CH_3 \rightarrow CH_2=CHCH_2CH_3 + HBr$	600	12.9[i]	45.6[i,k]	46.0	19.1	26.9	l
$CH_3CH_2CH_2CH_2Br \rightarrow CH_3CH_2CH=CH_2 + HBr$	670	12.9[i]	50.0[i]	50.4	16.8	33.6	l
$CH_3CH_2Cl \rightarrow CH_2=CH_2 + HCl$	700	13.4[i]	57.1[i]	57.1	16.5	40.6	l
$CH_3CHClCH_3 \rightarrow CH_3CH=CH_2 + HCl$	660	12.9[i]	49.0[i]	49.4	16.8	32.6	l
$CH_3CH_2CH_2Cl \rightarrow CH_3CH=CH_2 + HCl$	720	12.9[i]	53.5[i]	53.9	13.9	40.0	l
$(CH_3)_2CClCH_3 \rightarrow (CH_3)_2C=CH_2 + HCl$	590	12.4	41.4	42.0	16.2	25.8	l
$CH_3CHClCH_2CH_3 \rightarrow CH_3CH=CHCH_3 + HCl$	630	12.7[i]	47.6[i,k]	47.8	14.6	33.2	l
$CH_3CHClCH_2CH_3 \rightarrow CH_2=CHCH_2CH_3 + HCl$	630	12.9[i]	48.6[i,k]	49.0	16.8	32.2	l
$CH_3CH_2CH_2CH_2Cl \rightarrow CH_3CH_2CH=CH_2 + HCl$	720	12.9[i]	53.4[i]	53.8	14.0	39.8	l
$CH_2ICH_2I \rightarrow CH_2=CH_2 + I_2$	490	13.0	36.6	37.0	10.9	26.1	n
$I_2 + H_2 \rightarrow 2HI$	690	11.42	41.4	41.6			o,p
$CH_3CH_3 \rightarrow CH_2=CH_2 + H_2$	900	13.5[j]	≥70	≥70	32.1	≥38	p,q
$CH_3CH_2CH_3 \rightarrow CH_3=CHCH_2 + H_2$	870	13.0[j]	≥66	≥67	29.1	≥38	p,r
$(CH_3)_2CHCH_3 \rightarrow (CH_3)_2C=CH_2 + H_2$	870	13.0[j]	≥64	≥65	27.6	≥37	p,s
$\overline{CH=CHCH_2CH_2CH_2} \rightarrow \overline{CH=CHCH=CHCH_2} + H_2$	790	13.04	58.8	59.0	23.2	35.8	p,t
$\overline{CH=CHCH_2CH_2CH_2CH_2} \rightarrow$ $\overline{CH=CHCH=CHCH_2CH_2} + H_2$	760	13.0[j]	59.8	60.0	24.2	35.8	u
$Br_2 + H_2 \rightarrow 2HBr$	600	10.0[j]	≥31	≥31			p,v
$Cl_2 + H_2 \rightarrow 2HCl$	500	10.0[j]	≥26	≥26			p,v
$H_2{}^* + H_2 \rightarrow 2HH^{*g}$	900	10.0[j]	≥45, ≥47[h]	≥45, ≥47[h]			p,v
$H^*Br + H_2 \rightarrow HBr + HH^{*g}$	900	10.0[j]	≥42	≥42			p,v
$H^*Cl + H_2 \rightarrow HCl + HH^{*g}$	900	10.0[j]	≥43	≥43			p,v
$HBr^* + Br_2 \rightarrow HBr + BrBr^{*g}$	600	10.0[j]	≥19	≥19			p,v
$HCl^* + Cl_2 \rightarrow HCl + ClCl^{*g}$	600	10.0[j]	≥25	≥25			p,v

[a] T_m represents the mean temperature at which the reaction was studied. [b] Units of the A factors, sec.$^{-1}$. [c] Activation energy of forward reaction in kcal./mole at mean temperature, T_m. [d] Activation energy of forward reaction in kcal./mole estimated for the temperature 298 °K. [e] Standard internal energy change for the reaction at 298 °K. (kcal./mole). [f] Activation energy of the reverse reaction in kcal./mole at 298 °K. [g] Asterisk represents labeling that makes the two species distinguishable but chemically equivalent; for example, $H_2{}^*$ represents H_2, o-H_2, or p-H_2. [h] The lower limit for the activation energy of ortho–para H_2 exchange is 45 kcal./mole and the lower limit for H_2–D_2 exchange is 47 kcal./mole. [i] Adjusted value as indicated in ref. 3. [j] Assumed value. [k] There are two independent elimination paths with ratio of rates equal to 1:48 [A. Maccoll and R. H. Stone, *J. Chem. Soc.*, 2756 (1961)]. The values tabulated in this table are calculated from the measured total rate of elimination. [l] See ref. 3 and W. Tsang, *J. Chem. Phys.*, **41**, 2487 (1964). [m] P. S. Nangia and S. W. Benson, *ibid.*, **41**, 530 (1964). [n] M. J. Polissar, *J. Am. Chem. Soc.*, **52**, 956 (1930). [o] J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292, 1577 (1959). [p] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 258, 291, 292, 355. [q] K. T. Ivin and E. W. R. Steacie, *Proc. Roy. Soc.* (London), **A208**, 25 (1951). [r] E. W. R. Steacie and J. E. Puddington, *Can. J. Res.*, **16**, 411 (1938); M. W. Travers, *Trans. Faraday Soc.*, **33**, 751 (1937). [s] L. S. Echols and R. M. Pease, *J. Am. Chem. Soc.*, **58**, 1317 (1936); **61**, 208, 1024 (1939); R. N. Pease and E. S. Durgan, *ibid.*, **52**, 1262 (1930). [t] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948). [u] S. R. Smith and A. S. Gordon, *J. Phys. Chem.*, **65**, 1124 (1961). [v] Estimated from measured rate of rate-controlling step in radical mechanism.

At this point it would be appropriate to discuss the sensitivity of the calculated activation energy to variation in the distance parameters. A variation of 10% in the bond lengths r_{AA^*} and r_{BB^*} for the exchange reactions induces about a 12% change in the total activation energy. In the same system a 10% change in the distance r_e induces an 8% change in energy. The activation energy for the addition of AA^* to an olefin is very sensitive to the r_{AA^*} distance; a 10% change in this distance induces a 20% change in the activation energy. On the other hand, this energy is very insensitive to the bond length r_{BB^*}; 10% variation of this quantity results in only 3% variation in the energy. The 10% variation of r_e induces about a 9% change in the activation energy for the addition of AA^* to an olefin. In these calculations the exponent in the re-

pulsive potential was assumed to be 12 $(B/r^{12}{}_e)$. The variation in the total activation energy when this exponent is reduced to its lower limit of 9 is less than 6%.

The predicted activation energies are within an average of 1.3 kcal./mole of the observed values; the maximum deviation is 3.2 kcal./mole. This corresponds to an average deviation of 4% and a maximum deviation of 12%. These calculated values conform to the observed values over the reported range of 18–41 kcal./mole. Since we are also able to determine the heat of reaction, we can predict the activation energies for the reverse of the reactions listed. These likewise are in agreement with the reported data to within 3 kcal./mole over a much broader range of values, *e.g.*, 24–61 kcal./mole. There are many more reactions

of known activation energies which are structurally analogous to those listed that have not been considered here, because of their slight differences from the ones given. The consistency of this theory is remarkable, considering that the same rule for estimating the parameters of the transition state gave agreement for the addition reactions of HX and X_2 to olefins and the exchange reactions between X_2 and H_2.

An ambiguity exists in the interpretation of the kinetics of hydrogenation of 2,4-cyclopentadiene. The addition of molecular H_2 across either the 1,2 or 1,4 positions leads to the same product. The 1,4 type of elimination of molecular H_2 has been observed for 2,4-dihydrofuran,[12] while direct H_2 elimination from 2,3-dihydrofuran has never been observed. In our calculations it was assumed that the molecular H_2 added across the 1,2 position of cyclopentadiene. Excellent agreement between the calculated and the observed activation energy of hydrogenation of cyclopentadiene was found. The stepwise heats of hydrogenation of cyclopentadiene to 2-cyclopentene to cyclopentane are 24.0 and 26.9 kcal./mole, respectively,[13] indicating a near equivalence of the double bonds. This situation does not exist for furan, where the heat of hydrogenation of the first step is apparently

(12) C. A. Wellington and W. D. Waiters, *J. Am. Chem. Soc.*, 83, 4888 (1961).
(13) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *ibid.*, 59, 831 (1937); G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, 58, 146 (1936).

one-third the heat of the second step. While it would appear that the H_2 is adding 1,2 to cyclopentadiene, further investigation of the difference in the transition states of the two hydrogenation paths is now in progress.

V. Ionic States in Olefin Chemistry

One of the very interesting aspects of the present calculation is the astonishingly low energies required to produce semi-ion pair states in the olefins. From Tables III, V, and VI we see that only 14.5 kcal. is required to produce a semi-ion pair in C_2H_4 while half of this, only 7.5 kcal., is needed to do the same in i-C_4H_8. These energies are the least subject to error of all of the quantities that we have calculated and do not depend in any way on the model or the oversimplification of the charge density distribution. It seems to us that these low polarization energies must be intimately connected with the important kinetics of nucleophilic and electrophilic reactions at double bonds. They are also an indication that the ground states of olefins may already contain an important fraction of "ionic" character. In the aromatic family we believe that this can be demonstrated. We also believe that the *meta–ortho–para* directing effect of substituents in aromatic rings is a direct stabilization of the relevant semi-ion pair state by electrostatic polarization. In this sense it is closely related to the Markovnikov rule observed for the olefins. We hope to deal with this further in a future publication.

Magneto-optical Rotation Spectra of
Porphyrins and Phthalocyanines

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Contribution from the Engineering Physics Laboratory, Experimental Station, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. Received April 15, 1965

The magneto-optical rotation (m.o.r.) spectra of a number of porphyrins, phthalocyanines, and their metal derivatives were determined in an effort to correlate m.o.r. spectra with absorption spectra. Of the compounds studied, zinc and magnesium phthalocyanine had the largest magnetic rotations: -8×10^5 and -8.8×10^5, respectively. No evidence could be obtained for relationships between the shape or the magnitude of the observed magnetic rotations and the ground-state para- or diamagnetism of the molecules. Some evidence was obtained for a relation between the shape of the m.o.r. spectrum and the polarizations of transitions in the absorption spectra. A description is given of an automatic recording m.o.r. spectropolarimeter with a solvent-compensating feature and a sensitivity of ± 0.001 and $\pm 0.003°$ for the visible and ultraviolet regions, respectively, of the spectrum.

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Introduction

A study of the magneto-optical rotation (m.o.r.) spectra[2] of a number of porphyrins, phthalocyanines, and their metal derivatives was carried out in an effort to obtain experimental evidence for relationships of m.o.r. to absorption spectra. The porphyrins and phthalocyanines as a group are very suitable for such investigations since they have the largest magnetic rotations observed to date and are well characterized spectroscopically.[3]

In magneto-optical rotation spectroscopy, a magnetic field is used to induce an optical rotation (Faraday effect) in a molecule. The variation of this magnetically induced optical rotation with wave length gives an "m.o.r. spectrum." In a previous paper,[4] five general

(2) V. E. Shashoua, *J. Am. Chem. Soc.*, 82, 5505 (1960).
(3) (a) M. Gouterman, *J. Mol. Spectry.*, 6, 138 (1961); (b) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.
(4) V. E. Shashoua, *J. Am. Chem. Soc.*, 86, 2109 (1964).