ticles and polymer matrix are similar in chemical composition, as evidenced by infrared analysis and close correspondence in refractive index. The particles, therefore, have a higher density and a smaller thermal expansion coefficient than the melt, since a small increase in refractive index is proportional to a small increase in density.[19]

The observed average diameter of the crosslinked networks is about 10 μ and corresponds to a "molecular weight" of about 10^{14} assuming them to be solid spheres with a density of 1 g./ml. A random coil with radius of gyration 5 μ would have molecular weight 3×10^9.[20] This estimate is low since crosslinking will have the effect of decreasing the particle radius below that of a random coil. In any case, the experiments demonstrate the inappropriateness of including the "molecular weights" of these particles in the distribution for the uncrosslinked polymer molecules, since the resulting weight average molecular weight reflects no contribution from the major part of the polymer.

The particles observed by phase contrast microscopy and small angle light scattering are much larger than those with diameter 500 Å. reported in a study of polyethylene by electron microscopy.[5]

The crosslinked networks are precipitated by ultracentrifugation in *n*-decane. The amount of precipitate is approximately the same as the volume fraction of crosslinked networks derived from phase contrast observations on films. However, viscosity measurement indicates that the ultracentrifuge residue contains other polymeric material in addition to the crosslinked networks, such as branched molecules of high molecular weight.

The small angle light scattering experiments show that no information about the weight average molecular weight of the polymer can be obtained from measurements in the angular range above 25° when crosslinked networks are present even in small amounts. The intensity of light scattered from the network particles outweighs by far that from the branched polymer molecules, especially at small angles. There is no obvious way of separating the simultaneous scattering of the two species.

Fawcett-type polyethylene is characterized by extensive long chain branching.[2,3] The long branches are formed by chain transfer to polymer in the polymerization process.[21] However, chain transfer alone can result neither in an infinite branched molecule nor in a crosslinked network.[22] An additional reaction, such as intermolecular or intramolecular recombination of pairs of branched radicals,[23] is required for the formation of crosslinked networks.

Acknowledgment.—The authors gratefully acknowledge the background provided by C. K. Sloan, C. H. Arrington, Jr., and W. H. Aughey in the respective fields of angular dependence light scattering technique, theoretical approximations and instrumentation. The pioneering work of E. J. Hennelly laid the foundations for the successful application of these methods to polyethylene.

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(19) (a) H. A. Lorentz, "Theory of Electrons," Teubner, Leipzig, 1909; (b) J. H. Gladstone and T. P. Dale, *Phil. Trans.*, **153**, 317 (1863); (c) J. F. Eyckman, *Rec. trav. chim.*, **14**, 177 (1895); (d) E. Jenckel, *Kolloid-Z.*, **120**, 160 (1951).

(20) J. T. Atkins, L. T. Muus, C. W. Smith and E. T. Pieski, THIS JOURNAL, **79**, 5089 (1957) (Paper IX).

(21) (a) P. J. Flory, THIS JOURNAL, **69**, 2893 (1947); (b) J. K. Beasley, *ibid.*, **75**, 6123 (1953) (Paper IV).

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WILMINGTON, DELAWARE

[CONTRIBUTION NO. 5205 FROM THE DIVISION OF APPLIED CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Electronic Structure and Reactivities of Monoölefins

BY S. SATO[1] AND R. J. CVETANOVIĆ

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LCAO-MO method with the inclusion of overlap integrals between adjacent orbitals and with the assumption of hyperconjugation was applied to calculate the free valences, excitation energies, atom and bond localization energies, bond orders and electron densities of a number of monoölefinic hydrocarbons. These quantities were compared with the relative rate constants of addition reactions with methyl, ethyl and trichloromethyl radicals (radical reagents) and of oxygen atoms (^3P), peracetic acid, bromine and dibromocarbene (electrophilic reagents). For the reactions of the radical reagents the logarithms of relative rate constants were found to be roughly linearly related to the free valences and for the reactions of the electrophilic reagents good correlations were obtained with the excitation energies and the bond orders. In the former case a statistical factor of one-half was applied to the rate constants of symmetrical olefins.

Introduction

Attempts to correlate trends in chemical reactivity with various quantities which can be derived by the application of the molecular orbital theory have met with considerable success in spite of the crude approximations which have to be made in order that the calculations can be carried out. So far the same approach has been applied to olefins only to a relatively limited extent.

In the present paper the concept of hyperconjugation, originated by Mulliken and his co-workers,[2] is employed to calculate the free valences, excitation energies, atom and bond localization energies, bond orders and electron densities for a number of monoolefins. These quantities are compared with the literature values for the experimentally observed trends in the rates of addition to the olefinic double bonds of (a) methyl, ethyl and trichloromethyl radicals (radical reagents) and (b) bromine, bromocarbene, peracetic acid and ground state

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(1) National Research Council Postdoctorate Fellow, 1956-1958.

(2) R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL **63**, 41 (1941).

TABLE I

RELATIVE RATE CONSTANTS (k) FOR DIFFERENT SERIES OF ADDITION REACTIONS TO OLEFINS (GROUP A, RADICAL REAGENTS)

Type of substitution	Olefin	CH_3[a]	C_2H_5[b]	CCl_3[d]	Olefin	CH_3
0	Ethylene	0.94				
α	Propylene	.61			$PhCH{=}CH_2$[g]	0.73
	1-Butene	.75		0.19		
	1-Pentene	.68				
	1-Hexene	.71	0.43			
	1-Nonene	.61		0.19[e]		
αα	Isobutene	1.00	1.00[h]	1.00	$Ph_2C{=}CH_2$	1.00
	2,3,3-Trimethyl-1-butene		0.48			
αβ	*cis*-2-Butene	0.094			$PhCH{=}CHPh$[h]	0.092
	trans-2-Butene	0.19	≤ .04[c]	0.15[f]		
	Cyclohexene		< .09	.045		
ααβ	2-Methyl-2-butene			.17	$Ph_2C{=}CHPh$	.038
ααββ					$Ph_2C{=}CPh_2$	.011
	1,3-Butadiene			>38		

[a] R. P. Buckley, F. Leavitt and M. Szwarc, THIS JOURNAL, **78**, 5557 (1956). [b] D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc.* (*London*), **A244**, 297 (1958); rate constant of reaction with 2,4,4-trimethyl-1-pentene is taken as unity in this series. [c] *trans*-4-Octene. [d] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949). [e] 1-Octene. [f] Cyclopentene. [g] Ph = Phenyl radical. [h] Mixture of *cis* and *trans*. [i] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, **77**, 5493 (1955).

oxygen atoms (electrophilic reagents). The respective relative rate constants for these two groups are summarized in Tables I and II, taking in both cases the rates for an α,α-substituted olefin as unity. The reactions of the electrophilic reagents show a continuous increase in rates with the number of alkyl radicals directly attached to the doubly bonded carbon atoms. They also give linear free energy (log k − log k) plots[3,4] as well as linear log k plots against some physical properties of the olefins[4] (ionization potentials, spectroscopic excitation energies, heats of hydrogenation). The trends in the rates of the reactions of the radical reagents on the other hand appear to be much more irregular.

TABLE II

RELATIVE RATE CONSTANTS (k) FOR DIFFERENT SERIES OF ADDITION REACTIONS TO OLEFINS (GROUP B, ELECTROPHILIC REAGENTS)

Type of substitution	Olefin	$O(^3P)$[a]	Peracetic[b] acid	Br_2[d]	CBr_2[e]
0	Ethylene	0.038	0.002	0.18	
α	Propylene	.23	.046	0.36	
	1-Butene	.24	.047		
	1 Octene		.054		0.07[f]
	1-Decene		.051		
αα	Isobutene	1.00	1.00	1.00	1.00
αβ	*cis*-2-Butene	0.84	1.01[c]		
	trans-2-Butene	1.13			
	cis-2-Pentene	0.90	1.03[c]		
	2-Hexene		1.08[c]		
	3-Hexene		1.40[c]		
	3-Heptene		1.20[c]		
	4-Nonene		1.14[c]		
	Cyclobutene		0.22		
	Cyclopentene	1.20	2.12		0.5
	Cyclohexene		1.40		0.4
	Cycloheptene		1.90		
ααβ	2-Methyl-2-butene		13.5	1.9	3.2
	1-Methylcyclopentene		24.1		
ααββ	2,3-Dimethyl-2-butene	4.18	Very fast	2.5	3.5
	1,3-Butadiene	0.95[g]			0.5

[a] R. J. Cvetanović, *J. Chem. Phys.*, **25**, 376 (1956); **30**, 19 (1959). [b] J. Böeseken and J. Stuurman, *Rec. trav. chim.*, 56, 1034 (1937); J. Böeseken and C. J. A. Hanegraaf, *ibid.*, 61, 69 (1942); D. Swern, THIS JOURNAL, 69, 1692 (1947). [c] Mixture of *cis* and *trans*. [d] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984, 1396 (1935). [e] P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956). [f] 1-Hexene. [g] R. J. Cvetanović, to be published.

Although the concepts of electrophilic, nucleophilic and homolytic reactions are based on the well known simple assumptions regarding the number of electrons donated by each of the two reactants for the formation of new bonds, the criteria for classification of reagents must ultimately be based on the experimentally observed trends in rates under specific conditions. In some cases then there is need for a quantitative modification of the original concepts. Thus chlorine atoms appear to be strongly electrophilic and some free radicals can exhibit electrophilic or nucleophilic character in certain reactions.[5] Similarly, ground state oxygen atoms, which are diradicals, behave as electrophilic reagents in their reactions with olefins.[4] There is evidently room for gradations between the extreme cases, and it appears correct to speak of the degree of homolytic and electrophilic or nucleophilic character of a reagent in a reaction.

The types of correlation to be expected for the rates of reactions of heterolytic and homolytic reagents with unsaturated hydrocarbons have been discussed in particular by Burkitt, Coulson and Longuet-Higgins.[6] The initial stages of heterolytic reactions ought to be governed mainly by the coulombic forces between the existing or induced charges, while the ease of radical reactions should be determined by the free valence of the reactive center of the unsaturated hydrocarbon. Thus for the reactions of methyl radicals with a number of aromatic hydrocarbons Coulson found[7] a good linear correlation of the logarithms of the rate constants with the free valences or the localization

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(3) P. S. Skell and A. Y. Garner, THIS JOURNAL, **78**, 5430 (1956).

(4) R. J. Cvetanovic, *J. Chem. Phys.*, **30**, 19 (1959).

(5) G. A. Russell, THIS JOURNAL, **80**, 4987 (1958); R. L. Dannley and M. Sternfeld, *ibid.*, **76**, 4543 (1954); R. A. Benkeser and W. Schroeder, *ibid.*, **80**, 3314 (1958).

(6) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

(7) C. A. Coulson, *J. Chem. Soc.*, 1435 (1955).

energies, the last two quantities being linearly related between themselves for these hydrocarbons. Szwarc, who with his co-workers was responsible for the experimental values of the relative rate constants employed by Coulson, discussed further examples of similar correlations.[8]

The trends in the rates of reaction of methyl radicals with some olefins, on the other hand, appeared to exhibit irregularities suggestive of steric hindrance. The irregularities were ascribed to variations in the steric factors.[9] A potential importance of variable steric factors has been discussed also by James and Steacie[10] who studied the reactions of ethyl radicals with some olefins.

In the present work the expected correlations with the computed excitation energies are found for the heterolytic reactions (group B). In addition similar correlations are also exhibited by the bond orders of the olefinic double bonds. For the homolytic reactions (group A) a reasonably good correlation is found between the logarithms of the rate constants (after multiplications by a factor of $^1/_2$ for symmetrical olefins) and the free valences of the "reactive centres" of the monoölefins. Possible significance of these correlations is discussed.

The Method of Calculation and the Results

The calculations have been based on the molecular orbital treatment with the inclusion of overlap integrals between adjacent atomic orbitals, as described by Lofthus.[11] For all carbon atoms the value of the parameter[12] δ_{CC} has been assumed to be zero and $\delta_{H3} = \delta_{H2} = -0.50$.[13] The bond lengths for all C=C bonds have been assumed to be 1.353 Å. and of all C—C bonds 1.543 Å. The values of the overlap integrals listed have been taken from Lofthus[11]: $S_{CC}(1.353) = 0.264$, $S_{CC}(1.543) = 0.191$, and $S_{CH_3} = S_{CH_2} = 0.626$. The energies are computed[14] in units of β_0, the resonance integral for an assumed standard C=C bond (1.353 Å.). In the present work 1-butene has been treated as  $H_3{\equiv}C{-}\underset{\underset{\displaystyle H_2}{\|}}{C}{-}CH{=}CH_2$, *i.e.*, as a system of six π-electrons parallel to each other, and not as identical with propylene. Similar treatment was applied to the other olefins. Parallelity of all π-electrons in such systems is a crude approximation. However, the differences found between the conjugative effects of CH_3 and C_2H_5 radicals are very small, the former being slightly greater, as expected.

The excitation energies E_{exc}, the bond localization energies[15] E_{bl}, the atom localization energies E_{al}, the electron densities (q) and bond orders[16](p) of monoölefins have been calculated in the usual manner. Free valences (F) have been calculated from the equation,[17] $F = 4.732 - \Sigma p$, where Σp is the sum of bond orders of all the bonds from the atom under consideration. Bond orders of unity have been assumed for the C–H bonds which do not participate in the conjugation.

The computed excitation energies and the atom and bond localization energies are summarized in Table III. The case of 1,3-butadiene, in which only the ordinary conjugation is considered, has been included for comparison.

Bond Localization Energies.—As is shown in Table III, the stabilization energy obtained by substituting hydrogen atoms on ethylene successively with methyl radicals is almost constant per radical and independent of the position of substitution, *i.e.*, the stabilization energy for α,α-substitution is nearly the same as for α,β-substitution. This fact has been pointed out already by Coulson and Crawford on the basis of similar calculations.[18] Moreover, Table III shows that the effects of methyl and ethyl radicals are almost the same, although methyl radicals are slightly more effective than ethyl radicals.

Excitation Energies.—Since electron spin is not considered in the construction of the wave functions of molecular orbitals, the excitation energies shown in Table III represent the difference between the energies of the ground states and the averages of the singlet and triplet excited states.[19]

TABLE III

CALCULATED EXCITATION ENERGIES AND ATOM AND BOND LOCALIZATION ENERGIES (UNIT: $-\beta_0$)

Type of substitution	Olefin	Excitation energy ($E_{exc.}$)	Atom localization energy (E_{al})	Bond localization energy (E_{bl})	E_{bl} per radical
0	Ethylene	2.1498	1.5822	0	
α	Propylene	2.0182	1.5336	0.03194	
	1-Butene	2.0113	1.5301	.03156	
$\alpha\alpha$	Isobutene	1.9164	1.4854	.06270	0.03135
$\alpha\beta$	2-Butene	1.9022	1.5658	.06408	.03204
	2-Pentene	1.8975	1.5623[b]	.06370	.03185
	Cyclobutene[a]	1.9354			
	Cyclopentene[a]	1.8848			
	Cyclohexene[a]	1.8949			
$\alpha\alpha\beta$	2-Methyl-2-butene	1.8100	1.5177	.09504	.03168
$\alpha\alpha\beta\beta$	2,3-Dimethyl-2-butene	1.7242	1.5490	.12628	.03157
	Butadiene	1.4535	1.3897	.09035	

[a] Calculated on the assumption that all the π and quasi-π-electrons are parallel. [b] Atom localization energy at the ethyl radical substituted carbon atom is 1.5654.

Crawford calculated these values using $\delta_{H_3} = -0.5$ for the united H_3 atoms and $\delta_{CC} = -0.1$ for the carbon atoms adjoining the united atoms.[20] His results are, of course, linearly correlated with the results in Table III, which provides in addition the values for trimethylethylene, not considered by Crawford.

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[8] M. Szwarc, *J. Phys. Chem.*, **61**, 40 (1957).

[9] R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A240**, 396 (1957).

[10] D. J. L. James and E. W. R. Steacie, *ibid.*, **A244**, 297 (1958).

[11] A. Lofthus, THIS JOURNAL, **79**, 24 (1957).

[12] The symbols are defined in the quoted literature.

[13] Lofthus used alternately 0, −0.25 and −0.50 for δ_{H_3} and δ_{H_2} in similar calculations[11] and showed that the use of these different values did not lead to any essential differences in the results. Propylene was the only monoölefin for which calculations were carried out.

[14] The solutions have been obtained on an electronic computer. The authors are thankful to Dr. J. L. Howland of the Computing Devices of Canada Ltd. for devising a suitable numerical technique for problems of this kind.

[15] C. A. Coulson, *Research*, **4**, 307 (1951).

[16] B. H. Chirgwin and C. A. Coulson, *Proc. Roy. Soc.* (*London*), **A201**, 196 (1949).

[17] C. A. Coulson, "Valence," Clarendon Press, Oxford, London, 1953, p. 254.

[18] C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

[19] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

[20] V. A. Crawford, *J. Chem. Soc.*, 2061 (1953).

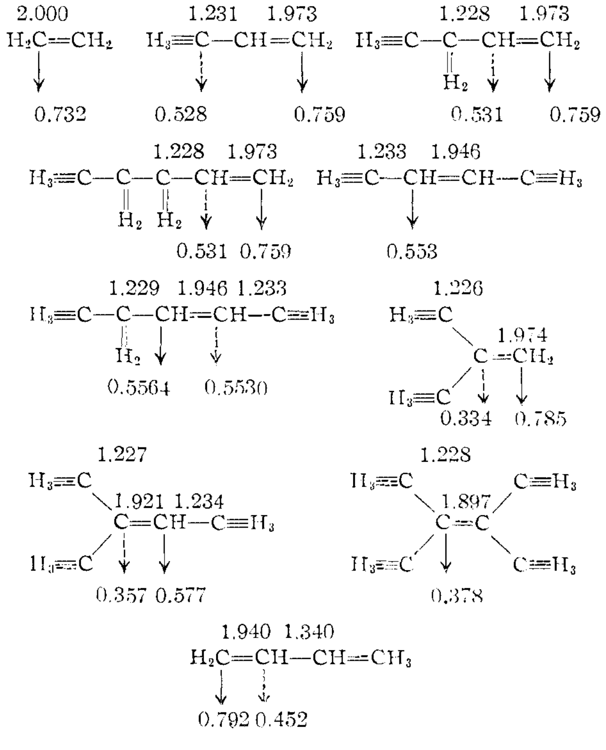
The excitation energy of 1,3-butadiene is much smaller than those of monoölefins. The excitation of 1,3-butadiene, however, is essentially different from that of monoölefins: in the excited state of 1,3-butadiene the double bond character is concentrated in the 2,3-CC bond rather than in the original 1,2- and 3,4-positions. In monoölefins, on the other hand, there is no comparable shift.

Atom Localization Energies.—Unsymmetrical monoölefins have two different values of atom localization energy and the smaller values only are shown in Table III. The smaller value always appears on the side of the less substituted carbon atom of the double bond, probably because the space for the resonance of electrons remaining after the localization is larger in this case than when the localization takes place at the more substituted carbon atom. Similarly in the case of 2-pentene the atom localization energy at the carbon atom to which a methyl radical is attached is slightly smaller than that at the other carbon atom of the double bond to which an ethyl radical is attached. This result suggests that the olefinic carbon atom to which methyl radical is attached should be slightly more reactive. However, some other factors may have to be considered also, as will be discussed later.

Free Valences and Bond Orders.—Table IV shows the results of computations of the free valences and the bond orders of aliphatic monoolefins. With the exception of 2-pentene, the carbon atom which gives smaller atom localization energy has larger free valence than the other carbon atom of the double bond. However, the values of these two quantities—the atom localization energy and the free valence—are not linearly related as was found by Coulson[7] to be the case for certain aromatic compounds.

TABLE IV

FREE VALENCES AND BOND ORDERS OF OLEFINS



Comparison with Experimental Data and Discussion

Rate of Reaction.—Because of paucity of experimental data and frequent difficulty of measuring activation energies accurately, the quantities calculated by the application of molecular orbital theory such as localization energies, free valences, etc., usually have been correlated with the logarithms of rate constants obtained at one temperature. It is regarded then that this procedure implies constant pre-exponential factors in the Arrhenius rate equation for the considered series of reactions and consequently that the logarithms of the reaction rate constants are proportional to the activation energies.[21]

In attempting to correlate the logarithms of the relative rate constants in Tables I and II with the various calculated quantities in Tables II and IV, it is found that the log k values for the reactions of group A, the radical reagents, are very roughly proportional to the free valences of monoölefins (Fig. 1). For the reactions of the electrophilic reagents, group B, they are proportional to the excitation energies or bond orders (Figs. 2 and 3). Here, the relative rate constants of the radical reagents with symmetrical monoölefins are divided by two before plotting their logarithms because these compounds have two equivalent carbon atoms in the double bond. For the reactions of the electrophilic reagents the relative rate constants are not divided by two because the excitation energies and bond orders are properties of a double bond as a whole and not of the two individual carbon atoms in the double bond.

The observed correlations for the electrophilic reagents are in agreement with the view that the rate-determining stage of the process of addition to monoölefins is an interaction of the attacking reagent with the double bond as a whole, as discussed previously.[4] In this case, at least the series of reactions of peracetic acid with the olefins considered here has constant entropies of activation[4] which is the basic requirement for theoretical correlations of this kind.[22]

The correlation with free valences which appears to hold for the additions of the radical reagents has to be regarded with some caution. Inasmuch as the free valence is considered to be an index of the potential free radical character at a particular position in a molecule, this correlation is the one which could be anticipated for attack by free radicals. In view of the observed correlation there would then be no need to assume lack of constancy of entropies of activation in the series in order to explain the seemingly irregular trends in the rates. Some support for this view is provided by the fact that the two radicals CH_3 and CCl_3, which differ considerably, give almost coin-

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(21) The relationship, log $k\alpha E$, where k is rate constant and E activation energy of the reaction, exists also when the pre-exponential factors are not constant but the series of reactions obeys the compensation rule. This matter has been discussed elsewhere.[4]

(22) A study of the temperature dependence of the rates of the corresponding series of the ground state oxygen atom reactions is in progress in this Laboratory.

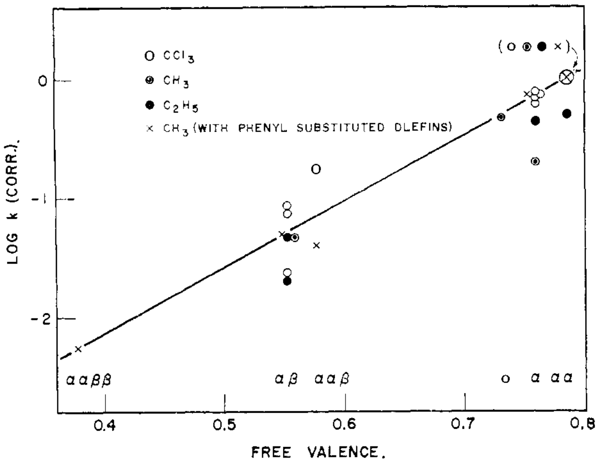

Fig. 1.—Plot of logarithms of corrected relative rate constants (*k* corr.) against the free valences of monoölefins for attack by free radicals. A statistical factor of $^1/_2$ has been applied to the experimental values of the rate constants in the case of symmetrical olefins.

cident plots of log *k* against the free valence of the olefins. At the same time, there is very little reliable experimental information on the temperature coefficients of the rates of such reactions and the relative importance of variations in the energies and entropies of activation remains uncertain. Moreover, even the available information on the rate constants at a single temperature is quite limited. For these reasons any discussion of the trends in the rates of these reactions has to be of a very tentative character until more extensive experimental information is accumulated.

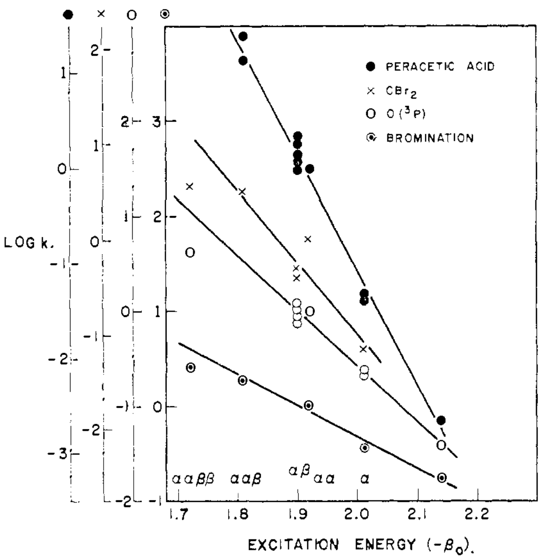

Fig. 2.—Plot of logarithms of relative rate constants against the excitation energies of monoölefins for attack by electrophilic reagents.

Linear correlations are not obtained if localization energies are plotted instead of free valences in Fig. 1. Free valence is considered to characterize the *localizability* of an atom in a conjugated system[23] and is, therefore, a property which comes into play in the initial stages of the reaction. The atom localization energy, on the other hand, is the energy necessary to localize one π-electron at an atom in a conjugated system. This idealized condition should correspond to a stage in the process subsequent to the activated state. The trends in the two quantities need not, therefore, be the same.

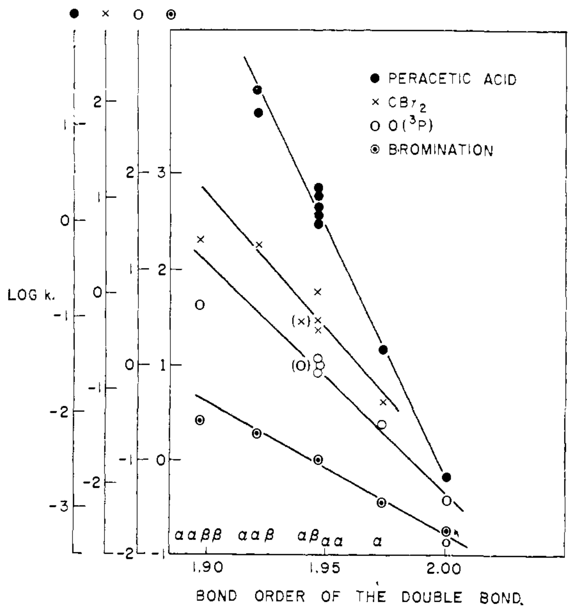

Fig. 3.—Plot of logarithms of relative rate constants against the bond orders of the double bond in monoölefins for attack by electrophilic reagents. The points in brackets on the O(^{3}P) and CBr$_2$ plots are for 1,3-butadiene.

The free valence of terminal atoms in 1,3-butadiene is larger than that in any monoölefin. This agrees with the fact that the relative rate constant of reaction of CCl$_3$ with 1,3-butadiene is larger than for the reactions with monoölefins. At the same time the value of log *k* as a function of the free valence for 1,3-butadiene deviates rather seriously from the linear plot in Fig. 1. However, the atom localization energy of 1,3-butadiene is much smaller than in the case of monoölefins and, perhaps, the reactivity should not be estimated on the basis of the initial stages of the reaction only.

For the reactions of the electrophilic reagents there is a good correlation between the excitation energies and the logarithms of relative rate constants, as shown in Fig. 2. This is the same kind of relationship as was pointed out by Szwarc in his discussion of the relative rates of addition of methyl radicals to some aromatic compounds.[8] However, in the present case the correlation is valid for electrophilic and not for radical reagents. It is of interest that the bond orders of monoolefins are also linearly related to log *k*, as shown in Fig. 3, although hitherto bond orders have not been directly correlated with the chemical reactivity. This quantity is considered to characterize the *bond strength* and may be intuitively associated with the relative *unreactivity* of the bonds in a series of structurally similar compounds.

The calculated bond order of terminal bonds of

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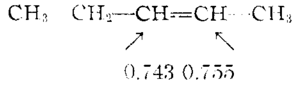
[23] R. D. Brown, *Quart. Revs.* (*London*), **6**, 63 (1952).

1,3-butadiene is 1.940 and the plot of log *k* against it fits into the linear plot in Fig. 3 for the oxygen atom and the bromocarbene additions, the two of the electrophilic reactions for which experimental values are available. The reactivity of butadiene is comparable with the reactivities of alkenes in the case of electrophilic reagents but is much greater for radical reagents. This readily differentiates the two types of reagents and has been utilized for that purpose.[24]

Position of Attack by the Reagents.—The results of the previous section indicate that in an olefin molecule the carbon atom which has the largest free valence should be most susceptible to attack by radicals such as CH_3, C_2H_5 and CCl_3. On the other hand, for additions of electrophilic reagents, *i.e.*, the reactions of group B, it is most likely that the double bond as a whole participates in the formation of the activated state which determines the rate of addition. This, however, does not necessarily imply three-membered ring intermediate or final products, although the latter are frequently formed: epoxides in the oxidation with peracetic acid, dibromocyclopropane derivatives in the reaction with CBr_2 and epoxides in the reaction with ground state oxygen atoms. In the last reaction, carbonyl compounds (aldehydes and ketones) isomeric with the epoxides, are also the major products.[25] A consistent explanation of the epoxides, aldehydes and ketones formed with the various olefins requires the assumption of an "open" intermediate with the oxygen atom localized on one of the two carbon atoms of the double bond. There is, therefore, a definite "orientation" in the addition of oxygen atoms to olefins: the atoms add almost exclusively to the less substituted carbon atom of the double bond. In agreement with this, the calculated π-electron densities are always found to be greater at the less substituted carbon atoms. It is then probably correct to assume that the electrophilic character of oxygen atoms is responsible for their addition at the position of highest electron density. Thus, for example, in the reaction of 1-butene with oxygen atoms, butanal is essentially the only carbonyl compound formed and methyl ethyl ketone is found only in very small amounts. The case of 2-pentene is of special interest. The products of the reaction of 2-pentene with oxygen atoms indicate addition of oxygen atoms to the carbon atom of the double bond to which the methyl radical is attached. However, calculations show that the two carbon atoms of the double bond have essentially the same π-electron density (1.012 and 1.013, respectively).

A better agreement with the experiment can be obtained by the application of the frontier electron theory[26] according to which the electrons in the highest energy level of the molecule are most likely to determine the chemical reactivity. The frontier electron densities have therefore been calculated for all the monoölefins for which the total π-electron densities were known. For all the monoölefins except 2-pentene, the trends obtained by the two methods were found to be coincident. In the case of 2-pentene, on the other hand, the frontier electron densities are



$$CH_3\ \ CH_2—\underset{\overset{\nearrow}{0.743}}{CH}=\underset{\overset{\nwarrow}{0.755}}{CH}—CH_3$$

which is in qualitative agreement with the experimentally observed orientation.

The very successful quantum mechanical treatment of Wheland[27] for predicting the reactive positions in aromatic compounds for attack by electrophilic, radical and nucleophilic reagents was based on the assumption that the energy requirements for these processes can be adequately deduced by localizing, respectively, 2, 1 or 0 π-electrons in the atomic orbital of the attacked carbon atom. In principle this treatment should be also applicable to the corresponding reactions with monoölefins. The calculations for the case of electrophilic reagents are shown in Table V, while for the radical reagents they have already been given in Table I as the atom localization energies. These calculations predict well the positions attacked by the reagents, but the localization energies show no general correlation with the logarithms of relative rate constants for either group of reactions. This is probably so because the idealized model with completely localized π-electrons, on which the calculations of atom localization energies are based, is too far removed from the activated state which determines the rates of these reactions. It is probable then, as has been suggested in a previous publication,[4] that the over-all rates of addition and the position of attack are in general not governed by the same factors.

Table V

Atom Localization Energies for Electrophilic Reagents (Unit: $-\beta_0$)

$CH_2=CH_2$	1.5822	$(CH_3)_2C=CH_2$	1.3988
$CH_3CH=CH_2$	1.4825	$(CH_3)_2C=CHCH_3$	1.4306
$CH_3CH=CHCH_3$	1.5146	$(CH_3)_2C=C(CH_3)_2$	1.4618

While the computations reported here were in progress, an interesting paper by Binks and Szwarc[28] was published in which good correlations were found between localization energies and the relative rates of addition of methyl radicals to restricted classes of terminal olefins. The present attempt to correlate with the free valences the rates of radical additions to alkenes in general is considerably wider in its scope but retains, of course, a tentative character until more extensive experimental information becomes available. The two correlations are not equivalent since for monoolefins the free valences and the localization energies are not in general linearly related.

The correlations found for the electrophilic reagents appear to be reasonably straightforward and agree with the empirical relationships observed

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before.[4] Detailed structural configurations of the activated states responsible for the rates and the orientational effects in the two groups of reactions are still highly uncertain and no attempt will be made to discuss them here.

OTTAWA, CANADA

[A CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Electronic Properties of Alkyl Groups. I. Dispersion and Induction Forces

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Electronic effects arising from the large variations in the polarizabilities of alkyl groups are considered. The magnitude of the dispersion energy existing between the alkyl group and the ring in alkyl benzenes is estimated, and it is concluded that this quantity in the series of alkyl groups, methyl, ethyl, isopropyl and *t*-butyl, varies over a range of about 4.5 kcal./mole. Polarizabilities play an important part in connection with the inductive effect ascribed to an alkyl group. The polar substituent constants, σ^*, for alkyl groups are evaluated in a system in which the purely inductive and polarizability effects are opposed. It is argued that these constants may not be generally applicable as measures of the electronic properties of alkyl groups in systems where, for example, the inductive and polarizability effects operate in the same direction. The behavior of the neo-pentyl group is explainable on the basis of its polarizability. It can be concluded that the dispersion and induction forces due to alkyl groups in molecules are at least in part responsible for variations in the apparent order of electron release by the alkyl groups.

It was observed by Baker and Nathan in 1935 that the inductive order of electron release (methyl < ethyl < isopropyl < *t*-butyl) of alkyl groups is apparently not followed in the kinetics of the reaction of *para*-substituted benzyl bromides with pyridine.[1] The inversion of the inductive order of electron release by alkyl groups has subsequently been observed in many other contexts and is termed the Baker–Nathan effect. The most popular explanation of the effect has for many years involved the concept of hyperconjugation.[2,3] Recently it has been pointed out that other factors may be of overriding importance, and various experimental evidence has been offered to show the importance of these other effects.[4–6] As evidence accumulates, however, particularly on the physical properties of alkyl-containing compounds, it appears that there is as yet no completely satisfactory picture of the properties of alkyl groups. In this series of papers some experimental results will be presented regarding the physical properties of alkyl-containing compounds which will, it is hoped, help to clear up certain questions which remain open at present. The purpose of the present paper is to point out that the dispersion force interactions and other effects arising from the polarizabilities of alkyl groups, factors which have been largely neglected, many be of considerable importance in determining their behavior as parts of larger molecules.

In considering the electronic energy of molecules, it is generally necessary to ignore the dispersion forces which operate between atoms in the same molecule, because the treatment of such forces would be too difficult. They are apparent, however, in determining the properties of the rare gases and of non-polar molecules.[7–9] Pitzer has applied the concept of dispersion forces to show that they may be of considerable importance when operating between atoms in the same molecule.[10,11] Schubert and Robins have considered polarizabilities in a qualitative sense in discussing the effect of the neo-pentyl group on spectral transition energies.[12]

The simple equation derived by London[7] to express the dispersion energy between two unlike atoms is

$$E = -\frac{3\alpha_1\alpha_2}{2r^6}\,\frac{I_1I_2}{I_1 + I_2} \qquad (1)$$

where α_1 and α_2 are the polarizabilities in cm.^{3}, I_1 and I_2 are the ionization energies and r is the internuclear distance in cm. In applying this expression to polyatomic systems as we do below it is necessary to make some rather gross approximations. Nevertheless when it is applied to molecules containing alkyl groups it is possible to gain some insight into an important effect in determining their behavior.

The systems to be considered first are the alkylbenzenes; the molecules are assumed to be in the vapor state. The alkyl group and the ring are considered as two "pseudo-atoms," and we evaluate the dispersion energy between these two. The polarizabilities of the alkyl groups are estimated by summing the bond polarizabilities,[13] taking only the components which lie in the plane of the ring. One-half of the polarizability of the C–C bond joining the alkyl group to the ring is taken as belonging to the alkyl group. Since the polarizability of the C–H bond is not far from isotropic, this procedure is quite satisfactory; the values so

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