able for stretching vibrations. Further argument suggests that this relationship probably holds also for the bending force constants.

Finally, we should like to point out the general applicability of these arguments to a wide number of phenomena. Linear relations between $\Delta H$ and $\Delta S$ are very important in organic chemistry. Taft has pointed out$^6$ that this condition is necessary if


the Hammett sigma relations are to hold. The empirical success of these relations may well be due to the same set of curious circumstances which leads to the observed linear relation between $\Delta S$ and $\Delta H$ for iodine complexes.

Acknowledgments.—Partial financial support from the National Science Foundation is gratefully acknowledged. It is a pleasure to acknowledge helpful discussions with Professors G. C. Pimentel and R. S. Mulliken.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 2, OHIO]

Electronegativity. I. Orbital Electronegativity of Neutral Atoms

BY JÜRGEN HINZE AND H. H. JAFFE

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Electronegativity is discussed on the basis of Mulliken's definition ($\chi = E_e + I_e$), which leads to the conclusion, that it is not a property of atoms in their ground state, but of atoms in the same conditions in which they are found in molecules, the valence state. Valence state promotion energies are calculated and reported for a large variety of states of the atoms and ions of the first and second period. Combining these promotion energies with ionization potentials and electron affinities yields the electronegativities of a number of valence states. It is found that electronegativity can be defined in this way only for bonding orbitals, and the term "orbital electronegativity" is suggested for the values listed. The calculated orbital electronegativities for $\sigma$ orbitals are found to be higher in every case than for $\pi$ orbitals, and to be linearly related to the amount of $\alpha$ character in the hybrid orbitals. As expected, the electronegativity increases with increasing $\alpha$ character of the orbital considered.

Electronegativity is a measure of the power of a chemically bonded atom to attract electrons to itself. This concept, first introduced by Pauling,$^1$ was rapidly accepted and many applications have been found in all fields of chemistry. Pauling set up a scale of electronegativities of the elements, by comparing the energy of the heteronuclear bond $A-B$ with the average, arithmetic$^2$ or geometric,$^3$ of the homonuclear bond energies of the molecules $A-A$ and $B-B$. With this method, no absolute values can be obtained, and because of the inherent uncertainties in thermochemical data this relative scale is somewhat indefinite. Despite these inadequacies, a wide variety of chemical phenomena have been reasonably explained by use of electronegativities.

The degree of electron transfer in the bond $A-B$ toward the negative atom may be regarded as good measure of electronegativity difference. Unfortunately, such electron transfer is not directly observable and calculations of electron distribution for any molecule is an involved problem in itself, even for simple molecules, and not a suitable method to use as a base for an electronegativity scale. Since such exact results are not available, several alternate scales of electronegativity have been proposed, based on various observable properties of molecules which are related to the electron distribution. Such properties are dipole moments,$^4$ force constants$^5$ and nuclear quadrupole resonance frequencies.$^6$ The accomplishments in this field have been carefully reviewed by Pritchard and Skinner.$^7$ The best theoretical definition of electronegativity is given by Mulliken,$^8$ based on the concept that the energy expended in going from the covalent molecule $A-B$ to the ionic states $A^+ - B^-$ and $A^- B^+$ is equal if $A$ and $B$ have the same electronegativity. Hence, he concludes$^9$ that the electronegativity of $A$ is proportional to

$$\chi^A = I_e^A + E_e^A$$

(1)

where $I_e^A$ and $E_e^A$ are the appropriate valence state ionization potential and electron affinity, respectively. Electronegativities obtained from equation (1) are, to a good approximation, proportional to Pauling's values.$^10$

Pauling$^1$ defined electronegativity as an atomic property and believes$^8$ that it is virtually constant, even for different oxidation states of any one element. Thus, he quotes electronegativities of iron as 1.8 (Fe$^{2+}$) or 1.9 (Fe$^{3+}$); of copper as 1.9 (Cu$^{+}$) or 2.0 (Cu$^{2+}$); and of tin as, 1.8 (Sn$^{2+}$) or 1.9 (Sn$^{4+}$).$^11$ This conclusion seems somewhat surprising on the basis of the Mulliken definition, since one hardly expects ionization potential and electron affinity, or even their sum, to be the same for different oxidation states, and, hence, demands closer examination, particularly because differences of electronegativities have been noted by many authors.

(5) W. Gordy, ibid., 14, 804 (1946).
(6) W. Gordy, ibid., 19, 792 (1951).

Bellugue and Daudel\textsuperscript{12} and Sanderson\textsuperscript{11} have discussed electronegativities for different oxidation states, but their approaches were hampered by lack of data. The distinct but related problem of the dependence of electronegativities on valence states of neutral atoms has been considered by Walsh,\textsuperscript{14} who concluded that the electronegativity of carbon increases in the order tetrahedral $<$ trigonal $<$ trigonal. Similarly, Wilmhurst\textsuperscript{15} inferred from n.q.r. frequencies that the electronegativity of halogens increases with increasing s character in its bonding orbital. This concept has been generalized by Bent\textsuperscript{16} and needs careful examination, as already pointed out by Pritchard and Skinner\textsuperscript{5}; this need has become even more urgent in view of the renewed interest in electronegativities.\textsuperscript{16-17} A start in this direction has already been made by Mulliken\textsuperscript{6} and Skinner,\textsuperscript{10} but the range of the valence states considered was insufficient to permit recognition of over-all trends.

**Theoretical Background.**—Since the electronegativity is a property of atoms in a molecule, the ionization potentials and electron affinities in equation 1 are not the values of the atoms in their ground states but of the same condition in which the atoms are in a molecule. The “atom in molecule” was defined by Van Vleck as valence state. It is not a stationary state nor even a non-stationary state but a statistical average of stationary states\textsuperscript{15} chosen so as to have as nearly as possible the same interaction of the electrons of the atom with one another, as they have when the atom is part of a molecule. The valence state can be considered as formed from a molecule by removing from one atom all the other atoms with their electrons in an adiabatic manner, i.e., without allowing any electronic rearrangement. This state has been discussed in many places in the literature\textsuperscript{11,12} and needs no further explanation.

Two useful methods have been suggested for the calculation of valence state energies, one by Moffitt,\textsuperscript{22} extended by Companion,\textsuperscript{23} and the other by Van Vleck\textsuperscript{18} and Mulliken.\textsuperscript{8} Moffitt expresses the valence state energy as an appropriate linear combination of spectroscopic state energies. Mulliken’s method is based on Slater’s\textsuperscript{24} treatment of the many electron atom, in which the energy $W$ of any spectroscopic state is given by

$$W = \sum_i I_i + \sum_{i<j} \sum_k a_{ij} R_{ik} - \sum_{i<j} \sum_{k} b_{ik} b_{jk}^* G_{ik}$$

(2)

For the energy of a valence state, use of equation 2 is quite analogous to its more general application for spectroscopic states. In both cases the same integrals over the radial part of the wave function, $I$, $F$, and $G$, arise, while the $a$’s and $b$’s are easily evaluated and $b_{ij}$ the Kronecker $\delta$ is 0 when the spins of $i$ and $j$ are unequal and 1 when they are equal. Since the valence state is an average of these two alternatives, $b_{ij}$ is $\frac{1}{2}$. The two methods (Moffitt and Mulliken) are identical, provided just those spectroscopic states used in the Moffitt method are employed to evaluate the $F$’s and $G$’s in the Mulliken expression.

The Mulliken method was chosen for all our calculations for a number of reasons. (1) It lends itself much better to routine computation. (2) If one of the spectroscopic states needed to express the valence state energy is not observed, Moffitt’s method fails. (3) Configuration interaction is ignored in both methods; however, use of the largest possible number of states in the determination of the $F$’s and $G$’s is most likely to minimize the effect of configuration interaction,\textsuperscript{21} (4) Although the Moffitt method is reasonably straightforward for some simple valence states, it becomes very complex when hybrid orbitals are involved.

For the calculation of valence state ionization potentials $I_v$ and valence state electron affinities $E_a$, we require the corresponding values for the atomic ground states $I_g$ and $E_a$, respectively. The ground state ionization potentials $I_g$, usually obtained by extrapolation from spectral data, are listed by Moore\textsuperscript{26} (see Table I) and may be considered to be accurately known. Unfortunately, the ground states electron affinities, $E_a$, are not as readily obtainable,\textsuperscript{27} The best values were chosen

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Element & $I_g$ (eV) & $E_a$ (eV) \\
\hline
H & .747 & 12.595 \\
Li & .82 & 5.390 \\
Be & .19 & 9.320 \\
B & .33 & 8.296 \\
C & 1.12 & 11.256 \\
N & .05 & 14.535 \\
O & 1.465 & 13.614 \\
F & 3.48 & 17.418 \\
Ne & .57 & 21.569 \\
Na & .47 & 5.183 \\
Mg & .32 & 7.644 \\
Al & .22 & 5.984 \\
Si & 1.46 & 8.149 \\
P & .77 & 10.977 \\
S & 2.07 & 10.557 \\
Cl & 3.69 & 12.974 \\
\hline
\end{tabular}
\caption{Ground State Ionization Potentials $I_g$ and Electron Affinities $E_a$ (in eV)}
\end{table}


\textsuperscript{26} H. A. Skinner (Abstract of 18th International Congress of Pure and Applied Chemistry, Montreal, Canada, August, 1961) has made similar calculations including corrections for configuration interaction. Comparison of his data (private communication) with ours has shown that the differences rarely exceed 0.2 e.v.

\textsuperscript{27} H. O. Pritchard, Chem. Revs., 53, 529 (1953).
from papers by Edlen, Branscomb and Cubicciotti (see Table I). These electron affinities probably represent the most important source of inaccuracy in our calculations ($\approx 0.3$ eV). Such absolute errors, however, do not affect the valence state dependence of the calculated electronegativities.

The valence state ionization potentials and electron affinities are obtained by combining the valence state promotion energies of the atom, $P_0$, and of the positive and negative ion $P^+$ and $P^-$, respectively, with the ground state potentials $I^e = E_g + P^+ - P^-$, $E_r = E_g + P^+ - P^-$. Since $I^e$ is the energy necessary to remove an electron from the valence state, and $E_r$ the energy released by addition of an electron to this state, while the remaining electrons are not permitted to rearrange, the following transitions must be considered, using carbon as an example:

\[
\begin{align*}
\text{C}^- \xrightarrow{E_{0\sigma}} \text{C}(\text{te}^-) & \quad \text{C}(\text{te}^-) \xrightarrow{I_{0\sigma}} \text{C}^+(\text{te}^-) : \chi_{0\sigma}^* \\
\text{C}^- \xrightarrow{E_{1\sigma}} \text{C}(\text{tr}^2\pi) & \quad \text{C}(\text{tr}^2\pi) \xrightarrow{I_{1\sigma}} \text{C}^+(\text{tr}^2\pi) : \chi_{1\sigma}^* \\
\text{C}^- \xrightarrow{E_{2\sigma}} \text{C}(\text{tr}^2\pi) & \quad \text{C}(\text{tr}^2\pi) \xrightarrow{I_{2\sigma}} \text{C}^+(\text{tr}^2\pi) : \chi_{2\sigma}^* \text{ etc.}
\end{align*}
\]

(31) To prevent confusion of hybrids with pure s and p orbitals, the notation introduced by Mulliken [32] will be used throughout this paper; i.e., $te$ tetrahedral = $(sp)^4$, $tr$ trigonal = $(sp)^3$, $di$ digonal = $(sp)^2$.

(33) The notation that is used in Condon and Shortley, ref. 24.
(34) For most of the cumbersome calculations extensive use was made of an IBM 650 electronic computer and programs written by I. Goldfarb; Ph.D. Dissertation, Univ. of Cincinnati, 1959.
effective nuclear charge \(Z_{\text{eff}}\) which does not differ, according to Slater’s recipe, for configurations involving only s and p electrons. But, it has been shown that the Slater–Condon parameter are different for different configurations of the same atom. These differences must be ignored here, since it is not possible to obtain enough information from one configuration to calculate all the Slater–Condon parameters necessary to express a valence state energy. Thus, in configuration sp the spectroscopic state depends only on \(F_{sp}^a\) and \(G_{sp}^a\), but the energy of the valence state \(d^p\) involves also the integrals \(F_{sp}^b\) and \(G_{sp}^b\). Therefore, it was necessary to consider together the configurations \(sp^a\), \(sp^a\) respectively. Thus, in most cases, more multiplet levels are known than are needed to estimate the unknowns in equation 4, a least squares multiple regression method was used to obtain the best average values for the Slater parameters. For these elaborate calculations an IBM 650 was used. The energy levels to be fitted in this way have been obtained from Moore’s tables. Some of the data not tabulated have been obtained by extrapolation, using the straight line proportionality between the Mulliken and Pauling correlation coefficients. The equation found is

\[
W = W_0 + \sum c_i M_i \tag{4}
\]

where \(W_0\) is the constant term for configuration \(sp^a\), \(sp^a\), and \(sp^a\), respectively. Thus, \(n = 1\) if data of configuration \(sp^a\) are fitted and \(n = 1\) if data of configuration \(sp^a\) are fitted, otherwise, \(n\) and \(m\) are zero.

In Slater’s treatment many approximations are made, especially all configuration interaction is neglected. Consequently, equation 4 is not expected to represent the observed energy levels exactly. Since, in most cases, more multiplet levels are known than are needed to estimate the unknowns in equation 4, a least squares multiple regression method was used to obtain the best average values for the Slater parameters. For these elaborate calculations an IBM 650 was used. The energy levels to be fitted in this way have been obtained from Moore’s tables. Some of the data not tabulated have been obtained by extrapolation, using the straight line proportionality between the Mulliken and Pauling correlation coefficients. The equation found is

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The calculations described have been made for the elements of the first and second period up to their triply positive ions. For some of these elements no multiplet levels for the configuration \(p^+\) have been observed, and consequently \(\Delta W^p\) could not be obtained by the method described. The evaluation of these \(\Delta W^p\) was done by the following procedure. With the known \(\Delta W^p\) and the corresponding \(\Delta W^p\) a factor \(k\) was determined, so that

\[
k\Delta W_{kp} = \Delta W_{kp} \tag{5}
\]

This factor \(k\) shows little but steady variation in any one period. This permits a reliable extrapolation of the \(k\)'s corresponding to the unknown \(\Delta W^p\) values. Having determined the \(k\)'s, the \(\Delta W^p\)'s for the configuration \(2p^2\), \(3p^2\), \(3p^2\) have been estimated by equation 5.

**Evaluation of the Valence State Energy.**—For the expression of the valence state equation the equation 3 was used. The rather cumbersome evaluation of the factors \(c_i\) for the valence states was performed using an IBM 650. The \(F_i\)'s appearing in the valence state equation cannot be obtained explicitly, as shown above. It is, however, always possible to eliminate these \(F_i\)’s in terms of the \(W_i\)’s described. The evaluation of the promotion energies involving these eliminations and substitution of the Slater–Condon parameters into the valence state equation was also performed with the IBM 650.

Two methods appear feasible for the treatment of negative ions, for which calculations as described above cannot be done, since no spectroscopic data are available. One method is to extrapolate along a series of ionisation potentials of equivalent valence states of an isoelectronic sequence, using one of the procedures described. The other method involves extrapolation of promotion energies along a series of equivalent valence states of an isoelectronic sequence and, addition of the resultant promotion energy of the negative ion with the ground state electron affinity. Rohrlich has shown that the extrapolation involved in the second method is linear and hence the values obtained are more reliable, than those calculated by the first method in which the functional relation is open to considerable doubt. Consequently, \(P^+\) values were obtained by a least squares fit to the corresponding valence states \(P^+, P^{++}\) and \(P^{+++}\).

**Results**

The procedure described was used to calculate the orbital electronegativities for a wide variety of valence states of the elements of the first two rows of the periodic system. The promotion energies obtained for the states of the highest valence are given in Table II. The resulting orbital electronegativities with the corresponding valence state ionization potentials and electron affinities are given in Table III.

In the last column of this table the orbital electronegativities are transformed to values comparable with Pauling’s. Since the zero point of Pauling’s scale is arbitrary, there is no compelling reason to anticipate the previously reported direct proportionality between the Mulliken and Pauling scales, however, a linear relation must hold, if both definitions represent the same property. The correlation between the two scales was consequently obtained by fitting, by least squares, the best straight line to the selected electronegativities shown in Fig. 3. Values for those valence states were applied, which most probably correspond to the compounds used for the evaluation of Pauling’s electronegativities; these values are designated by asterisks in Table III. As seen in Fig. 3, the correlation is highly satisfactory and can be represented by

\[
0.168(\chi_m - 1.23) = \chi_p \tag{6}
\]

Based on the considerations outlined, it is possible to define electronegativity as a property only of bonding orbitals or other singly occupied orbitals.

(37) The program for this evaluation was written by Zung.
(39) The Slater–Condon parameters obtained, promotion energies, ionization potentials, electron affinities and electronegativities for states of lower valence, ionization potentials of lone pairs and electron affinities of vacant orbitals were obtained but are not reported here, owing to space limitations. These data are contained in an Air Force report, copies of which are available for distribution.
Fig. 4.—Electronegativity of carbon as a function of its character of the hybrid orbital. Dotted lines give electron affinity and ionization potential as function of its character of the hybrid orbital.

Lone pairs and electron holes (vacant orbitals) cannot be treated in the same manner, since here electron affinity and ionization potential, respectively, lose their meaning.

<table>
<thead>
<tr>
<th>TABLE II</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROMOTION ENERGIES (in eV.)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No. of val. electrons</th>
<th>Valence state</th>
<th>Li</th>
<th>Be*</th>
<th>B**</th>
<th>C***</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>s</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>1.647</td>
<td>3.658</td>
<td>5.997</td>
<td>8.002</td>
</tr>
<tr>
<td>(2)</td>
<td>sp</td>
<td>1.083</td>
<td>3.362</td>
<td>5.746</td>
<td>8.060</td>
</tr>
<tr>
<td></td>
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<td>2.284</td>
<td>3.768</td>
<td>12.137</td>
<td>17.020</td>
</tr>
<tr>
<td></td>
<td>dddi</td>
<td>6.800</td>
<td>2.702</td>
<td>4.674</td>
<td>6.565</td>
</tr>
<tr>
<td></td>
<td>trtr</td>
<td>1.362</td>
<td>4.845</td>
<td>7.433</td>
<td>10.431</td>
</tr>
<tr>
<td></td>
<td>tetr</td>
<td>1.884</td>
<td>4.599</td>
<td>12.074</td>
<td>17.106</td>
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<tr>
<td></td>
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<td>3.105</td>
<td>5.724</td>
<td>12.226</td>
</tr>
<tr>
<td>(3)</td>
<td>sp</td>
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<td>5.251</td>
<td>8.492</td>
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<tr>
<td></td>
<td>dir</td>
<td>4.164</td>
<td>8.576</td>
<td>13.030</td>
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<td>2.190</td>
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<td>B*</td>
<td>C</td>
<td>N*</td>
<td>O*</td>
<td>F***</td>
</tr>
<tr>
<td>(4)</td>
<td>sp</td>
<td>5.009</td>
<td>8.479</td>
<td>12.130</td>
<td>15.533</td>
</tr>
<tr>
<td></td>
<td>tete</td>
<td>3.043</td>
<td>6.386</td>
<td>9.224</td>
<td>12.519</td>
</tr>
<tr>
<td></td>
<td>C*</td>
<td>N</td>
<td>O</td>
<td>F*</td>
<td>Ne***</td>
</tr>
<tr>
<td>(5)</td>
<td>sp</td>
<td>0.982</td>
<td>1.082</td>
<td>1.830</td>
<td>1.941</td>
</tr>
<tr>
<td></td>
<td>dddi</td>
<td>4.965</td>
<td>7.967</td>
<td>10.390</td>
<td>13.116</td>
</tr>
</tbody>
</table>

It is interesting to note the extent to which the electronegativities obtained in this work depend on the character of the orbital. As may have been expected, the electronegativities for σ orbitals are considerably larger than those for the π orbitals. Also, the electronegativity increase with increasing s character anticipated by Walsh and Bent is borne out of the data observed.

An important feature is the linear relation observed between s character of the σ orbital and its electronegativity, which is shown in Figs. 4 and 5, where the electronegativities of the orbitals of the form

\[ \psi = \cos \alpha (s) + \sin \alpha (p) \]

are plotted against \( \cos^2 \alpha \) for C and N. This aspect
Orbital electronegativity of neutral atoms

**Table III**

<table>
<thead>
<tr>
<th>VALENCE STATE IONIZATION POTENTIALS: J, VALENCE STATE ELECTRON AFFINITIES Eα AND ORBITAL ELECTRONEGATIVITIES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Jr</strong></td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>H (1)</td>
</tr>
<tr>
<td>Li (1)</td>
</tr>
<tr>
<td>p</td>
</tr>
<tr>
<td>Be (2)</td>
</tr>
<tr>
<td>sr</td>
</tr>
<tr>
<td>ppp</td>
</tr>
<tr>
<td>didi</td>
</tr>
<tr>
<td>SP2PP</td>
</tr>
<tr>
<td>tetr</td>
</tr>
<tr>
<td>trtr</td>
</tr>
<tr>
<td>ete</td>
</tr>
<tr>
<td>tet</td>
</tr>
<tr>
<td>B (3)</td>
</tr>
<tr>
<td>ppp</td>
</tr>
<tr>
<td>did</td>
</tr>
<tr>
<td>trtr</td>
</tr>
<tr>
<td>di</td>
</tr>
<tr>
<td>trtrtr</td>
</tr>
<tr>
<td>C (4)</td>
</tr>
<tr>
<td>tetete</td>
</tr>
</tbody>
</table>
| C1, where use of d orbitals has frequently been made electronegativities of intermediately hybridized orbitals available by linear interpolation. Such intermediate hybrids are undoubtedly needed in compounds of N and O, probably of the halogens, where some hybridization is likely, and even in carbon. 40 Calculations for d orbital hybrids of second row elements have not been possible because of lack of spectroscopic data. These results would be of considerable interest, especially for the elements Si to Cl, where use of d orbitals has frequently been
Fig. 5.—Electronegativities of nitrogen and phosphorous as a function of s character of the hybrid orbital. Solid line, nitrogen; broken line, phosphorus.

postulated. Computations of electronegativities of positive ions are now in progress, and it is hoped that values for partially charged atoms may also be obtained.\(^{41}\) It was found in this Laboratory that these values are urgently required in order to get explanations\(^{45}\) for hybrid and ionic character of chemical bonds consistent with n.q.r. frequency changes and other molecular properties.

(41) Note added in proof.—Such values have been obtained and are in the process of publication.

Acknowledgments.—The authors wish to thank Dr. LI. A. Urhitehead and Sr. M. C. hlueller for many profitable discussions and the U. S. Air Force for financial support of the work reported.

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA]

Some Flash-photolytic and Photochemical Studies of Retinene and!Related Compounds\(^{18}\)

BY KARL-HEINZ GRELLMANN, RUDIGER MEMMING AND ROBERT LIVINGSTON

RECEIVED JULY 28, 1961

Flash illumination of air-free solutions of retinene produces a transient spectral response. The labile species, presumably the lowest triplet state of retinene, has a strong absorption band with a peak at 450 ma. It disappears by a first order process. The value of the rate constant depends on the solvent, being, at room temperature, 9.6 \(10^4\) sec.\(^{-1}\) for hexane and 4.3 \(10^4\) sec.\(^{-1}\) for glycerol. The rate decreases with temperature. The energies of activation are 0.9, 0.7 and 2.4 kcal. for hexane, toluene and glycerol, respectively. No spectral transients were observed when anaerobic solutions of a Schiff’s base, a protonated Schiff’s base or a hemiacetal of retinene were illuminated. Both the all-trans and the all-cis forms of the protonated Schiff’s base of retinene and propylamine undergo rapid cis-trans isomerization when they are exposed in methanolic solution to white light.

Introduction

Abrahamson, et al., report\(^2\) that flash illumination of all-trans retinene, in anaerobic tetrahydrofuran or methyl cyclohexane, produces a short-lived transient species, which disappears by a first order process. Neither vitamin A nor a protonated