range from 30 to 60° at the concentrations 0.001–0.00048 mole/l. Therefore, the integral intensities of the two bands can be considered to be proportional to the maximum intensity and the ratio x of the corrected maximum intensities of the two bands is proportional to the population ratio of the two molecular forms.

Let K be the constant of equilibrium of the two forms and a be a proportional constant independent of temperature and concentration. We have then

$$K = ax$$

The energy difference ΔE of the two forms can be calculated as

$$\Delta E = -RT_i \ln ax_i + T_i\Delta S$$
$$= -RT_i \ln x_i + T_i p$$

where x_i is the intensity ratio observed at the absolute temperature T_i, R the gas constant, ΔS the entropy difference between the two forms and $p = \Delta S - R \ln a$.

TABLE III

DATA USED FOR THE ESTIMATION OF THE ENERGY DIFFERENCE OF THE FOLDED AND THE EXTENDED FORMS OF AMn-LMA IN CCl_4 SOLUTION

Concn., mole/l.	Temp., °C.	Intensity of the 3387 cm.$^{-1}$ band	Intensity of the 3452 cm.$^{-1}$ band (cor.)	Intensity ratio, x (cor.)
0.00100	30	43.1	18.8	2.29
.00098	45	38.9	20.5	1.90
.00096	60	35.9	20.0	1.80
.00050	30	39.2	18.0	2.18
.00049	45	36.3	19.9	1.82
.00048	60	34.3	20.6	1.67

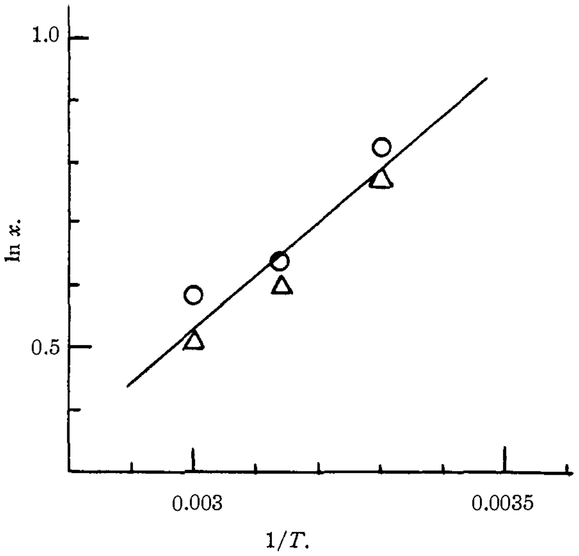

Fig. 6.—Ln x observed at different temperatures: ○, observed at about 0.001 mole/l.; △, observed at about 0.0005 mole/l.; —, determined by the method of least squares.

Using the experimental data shown in Fig. 6 and Table III (concentrations: 0.001 and 0.0005 mole/l., temperatures: 30, 45 and 60°), the energy difference has been calculated by the method of least squares as

$$\Delta E = -1.7 \pm 0.2 \text{ kcal./mole}$$

This difference arises from the energy of the *intramolecular* hydrogen bond of the folded form and also from the energy due to the difference of internal rotation state about the N–C and C–C single bonds.

TOKYO, JAPAN

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Nuclear Magnetic Resonance Absorption of Hydrogen in Methyl Groups. The Electronegativity of Substituents

BY A. L. ALLRED[1] AND E. G. ROCHOW

RECEIVED JUNE 3, 1957

The chemical shifts of the hydrogen atoms in the methyl groups of twenty-five compounds, both in the pure state and in infinitely dilute solutions in carbon tetrachloride, are reported herein. Also, chemical shifts are given for methyl chloride, methyl bromide and methyl iodide at varying concentrations in benzene, 2,2-dimethylpropane and carbon disulfide as solvents. Differences in the chemical shifts of these methyl halides (relative to water) in carbon tetrachloride, 2,2-dimethylpropane and carbon disulfide are shown to result largely from the change in bulk magnetic susceptibility of the solvent. The chemical shifts of hydrogen atoms obtained *at infinite dilution* for the methyl halides are found to be linearly related to the electronegativities of the halogens, and a qualitative order of electronegativities of the substituents in 21 other methyl compounds has been obtained by a reverse of this procedure.

Introduction

The basic equation for nuclear magnetic resonance is $\omega = \gamma H$, where ω is the resonance (or Larmor) frequency, γ is the gyromagnetic ratio, and H is the strength of the magnetic field at the nucleus in question. In a given external magnetic field, each nuclear species with a spin quantum number equal to one-half has a single characteristic resonance frequency which is the result not only of the imposed external field but also of perturbations caused by the magnetic shielding due to orbital (bonding) electrons and by the net bulk magnetic susceptibility of the sample. The change in resonant frequency due to changes in orbital electron environment, called the "chemical shift," often is difficult to separate from the change due to altered bulk susceptibility, yet the distinction must be made if conclusions about the polarity of the chemical bond are to be made. This paper describes an effort to separate the effects and, after demonstrating the validity of the method as applied to the

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[1] Natvar Corporation Fellow at Harvard University 1954–1956.

methyl halides, proceeds to apply it to other compounds containing methyl groups. A more detailed discussion of the several factors which affect the resonant frequency[2] need not be repeated here.

Experimental

In this research, the NMR spectra of liquid samples were observed at room temperature. A glass capillary, 1.1–1.8 mm. o.d., was filled with the reference compound water, sealed and placed inside a 5 mm. o.d. cylindrical Pyrex tube. The 5 mm. tube was filled to a height of 4.5 to 5.0 cm. with the sample and was sealed. Measurements by Bothner-By and Glick[3] showed that the magnetic susceptibility of the glass caused no observable change in the relative frequencies of the sample and the reference.

The spectra reported in Tables I and II were obtained with a Varian Associates V-4300 B high resolution nuclear magnetic resonance spectrometer in conjunction with a 12-inch electromagnet system. Resonance was observed at 40 megacycles. To average out some of the inhomogeneity inherent in the applied magnetic field and the inhomogeneity caused by imperfectly symmetrical sample cells, the sample was rotated 500–800 times per minute with an air turbine spinner. For measuring the difference in cycles of the NMR signals from the sample and from the reference, the side-band technique of Arnold and Packard[4] was adopted and a Hewlett–Packard Model 202A audio oscillator was used. Chemical shifts are reported as the resonance frequency of the methyl group minus the resonance frequency of water (CH_3–H_2O), and, therefore, increasing positive values of chemical shifts correspond to increasing applied fields if the radio frequency is constant. The accuracy of all measurements is estimated to be within ±0.7 cycle.

TABLE I

CHEMICAL SHIFTS OF METHYL HALIDES IN DIFFERENT SOLVENTS

	100% (cycles)	0% in CCl_4[a]	0% in CS_2[a]	0% in C_6H_6[a]	0% in $C(CH_3)_4$[a]	Vol. magnetic susceptibility × 10^6
CH_3F	84	21.3				
CH_3Cl	84.0	69.5	66.8	123.3	93.3	−0.548[14]
CH_3Br	81.0	84.1	78.6	138.8	110.2	− .783[14]
CH_3I	74.0	103.9	98.8	162.2	127.5	− .918[14]

[a] Chemical shifts in cycles (CH_3–H_2O), extrapolated to infinite dilution.

TABLE II

METHYL RESONANCES, CYCLES (CH_3–H_2O)

Compound	Pure liquid	0% in CCl_4
CH_3NO_2	47.5	19.2
CH_3F	84	21.2
$(CH_3)_2SO_4$	41.0	33.9
$(CH_3)_2CO_3$	54.3	40.6
$CH_3OC_6H_5$	73.2	43.8
CH_3COOCH_3	65.8	45.5
$(CH_3)_2SO_3$	59.1	48.3
$(CH_3O)_4Si$	60.1	49.0
$(CH_3O)_3B$	65.4	50.5
CH_3OH	74.0	55.6
CH_3OCH_3	105.1	62
CH_3Cl	84	69.5
CH_3COBr	85.9	79.1
CH_3Br	81	84.1
$CH_3COC_6H_5$	120	89.8
$CH_3C_6H_5$	130	98.6
CH_3I	80	103.9
$(CH_3CO)_2O$	121.6	103.9
CH_3COOH	127.5	107.6
$(CH_3)_2CO$	133.5	108.0
CH_3COOCH_3	131.3	111
CH_3CN	126	115.4
$CH_3C(NOH)CH_3$	. . .	119.3
$(CH_3)_3N$	127	. . .
$C(CH_3)_4$	174	153.9

The materials are commercial C.P. grade chemicals, with the exception of methyl fluoride which was prepared from methyl iodide and silver fluoride. The chemical shifts of the methyl groups of the pure compounds and of their solutions in carbon tetrachloride were measured. Usually five solutions of each compound were prepared, the concentration of each being known to ±0.4% by volume. For each compound, the chemical shift was plotted as a function of concentration, and the chemical shift *at infinite dilution* obtained by extrapolation as shown in Fig. 1. The chemical shifts of the compounds in the pure state and in infinitely dilute solution in carbon tetrachloride are presented in Table II. Methyl chloride, methyl bromide and methyl iodide also were observed in solutions in 2,2-dimethylpropane, carbon disulfide and benzene, and the data are presented in Table I.

Discussion

Correlation of Chemical Shift and Electronegativity.—In this research it has been found possible to correlate electronegativity and the chemical shifts of certain analogous compounds in infinitely dilute solutions in inert, magnetically isotropic solvents. As has been indicated in the more detailed discussion,[2] the relative contributions of parameters that influence the chemical shift of a substance change upon going from the pure substance to an infinitely dilute solution. The contributions may be considered separately: while the effect of bulk diamagnetic susceptibility on the chemical shifts of a series of pure compounds depends on the magnetic susceptibility of the medium, the contribution is constant in infinitely dilute solutions in a given solvent. The shielding by orbital electrons ordinarily does not vary with concentration, but if there are slightly different energy states due to association, contributions due to shielding by orbital electrons may change upon dilution. Aggregates formed by the release of energy of the magnitude of kT usually dissociate upon dilution. Thus hydrogen bonds and certain other weak bonds between groups capable of independent existence are broken, and the subsequent changes in the electronic environment of certain nuclei alter the chemical shifts. The association of certain atoms or molecules may also influence the field at a neighboring nucleus, not by direct electronic interaction through chemical bonds, but by magnetically anisotropic behavior. As an example, benzene associates with halogens through a "bond" perpendicular to the plane of the ring and appears to alter (as discussed later) the chemical shift due to the halogen atom in a methyl halide. This alteration might be attributable to diamagnetic shielding by electrons in a π-molecular orbital bond. However, due to the $1/d^3$ relation,[5] this contribution should be small. More probably, this alteration is due to the anisotropy of benzene. Since the magnetic susceptibility of benzene is abnormally large in the direction perpendicular to the plane of the ring,[6]

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[2] A. L. Allred, "Electronegativities of Carbon, Silicon, Germanium, Tin, and Lead," Thesis, Harvard University, 1956.

[3] A. A. Bothner-By and R. E. Glick, THIS JOURNAL, **78**, 1071 (1956).

[4] J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

[5] N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

[6] L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

preferred orientations of the ring with respect to a neighboring molecule in an applied field produce changes in the magnetic environment of the molecule.

At the start of this work Purcell suggested[7] that the use of "spherical" solvents might eliminate contributions due to magnetic anisotropy. The magnetic effects (other than bulk effects) of the magnetically isotropic and somewhat "spherical" solvents, carbon tetrachloride, sulfur hexafluoride and 2,2-dimethylpropane, are averaged to zero with time.

Several empirical analyses[8-11] of the chemical shifts exhibited by hydrogen indicated that as the electronegativity of substituents decreased, other factors remaining constant, the chemical shift usually increased. This trend was interpreted to reflect the electron density in the immediate vicinity of the nucleus of interest and the extent of magnetic shielding. The chemical shifts of hydrogen did not follow this trend as closely as might be expected from a consideration only of charge symmetry and the subsequent unimportance of paramagnetic shielding.[5] Contributions from magnetic susceptibility effects and from changes in hybridization might be expected to have greater relative importance in determining the chemical shifts of hydrogen than of the other elements, and the strong influence of hybridization is well illustrated by a comparison of the resonance of hydrogen atoms in ethane and ethylene with those of acetylene, which are relatively acidic (less shielded by electrons) but which exhibit a chemical shift intermediate between those of ethane and ethylene.[10]

Hydrogen NMR Spectra of the Methyl Halides in Carbon Tetrachloride.—In the methyl halides, the electron density around the hydrogen nuclei, and therefore the chemical shifts, should be a function of the electronegativity of the halogens, since no major change in the hybridization of the carbon-hydrogen bond occurs. For the pure methyl halides in the liquid state, the chemical shift (CH_3-H_2O), in cycles in an applied field of approximately 9400 gauss was observed to be 84 for methyl fluoride (measured by Meyer and Gutowsky[12]), 84 for methyl chloride, 81 for methyl bromide and 80 for methyl iodide. The last three values agree well with those reported by Meyer and Gutowsky.[12] This order is not consistent with predictions based on electronegativity.

The chemical shifts of the methyl halides were measured herein as a function of the concentration of methyl halide in carbon tetrachloride (Fig. 1). (Since methyl fluoride has a large vapor pressure at room temperature and all samples were observed in Pyrex tubes at room temperature, no investigation was made of methyl fluoride at concentrations greater than 9% by volume.) It is seen at once that the shifts of three of the halides vary in an extreme manner with dilution. By extrapolation in Fig. 1, the chemical shifts at infinite dilution in carbon tetrachloride as solvent are 21.1 for methyl fluoride, 69.5 for methyl chloride, 84.1 for methyl bromide, and 109.3 for methyl iodide. Thus upon dilution of the methyl halides in carbon tetrachloride, the *relative* magnitudes of their chemical shifts also changed in an extreme manner. The changes in the chemical shifts of the methyl halides upon dilution in carbon tetrachloride are attributed almost entirely to corresponding changes in the bulk diamagnetic susceptibility. For a series of compounds at infinite dilution in the same solvent, the effect of bulk magnetic susceptibility is, of course, constant. In Fig. 2, Huggins' electronegativity values[13] are plotted against the values of chemical shift (CH_3-H_2O), obtained by extrapolation, and it is apparent that the chemical shift of hydrogen in the methyl halides (at infinite dilution in carbon tetrachloride) is a linear function of the Huggins electronegativity of the halogen.

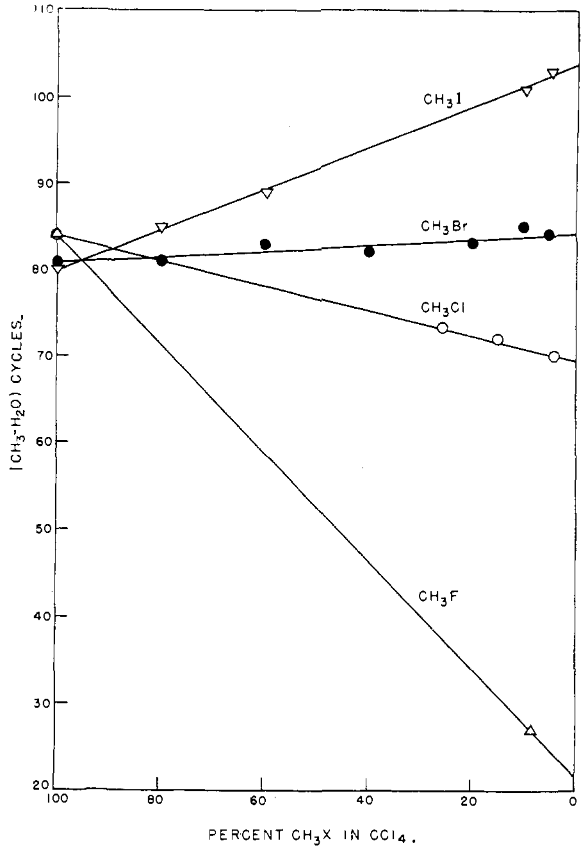

Fig. 1.—The effect of concentration on the chemical shift of the methyl halides in carbon tetrachloride.

Hydrogen NMR Spectra of the Methyl Halides in Other Solvents.—The NMR spectra of the methyl halides were further observed in 2,2-dimethylpropane (which is "spherical" and should be magnetically isotropic), in carbon disulfide (which is "cylindrical"), and in benzene (which

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[7] Private communication from E. M. Purcell to A. A. Bothner-By, R. E. Glick and L. N. Mulay.

[8] H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

[9] H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

[10] L. H. Meyer, A. Saika and H. S. Gutowsky, *ibid.*, **75**, 4567 (1953).

[11] B. P. Dailey and J. N. Shoolery, *ibid.*, **77**, 3977 (1955).

[12] L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953). The value for 9% concentration is an average value of the two peaks produced by hydrogen-fluorine spin coupling.

[13] M. L. Huggins, THIS JOURNAL, **75**, 4123 (1953).

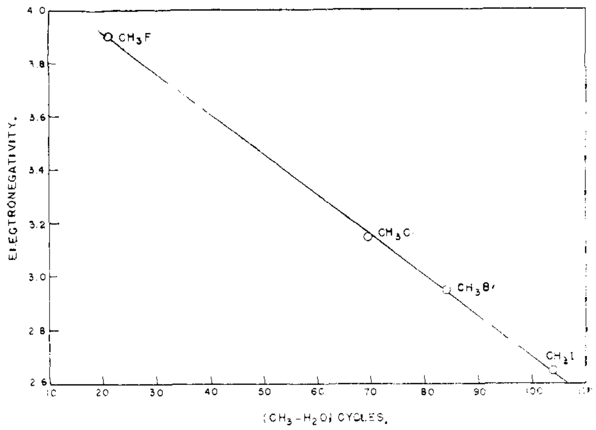

Fig. 2.—The effect of the electronegativity of the halogen on the hydrogen resonance frequency of the methyl group.

is "pancake-shaped" and magnetically anisotropic). The extrapolated values are recorded in Table I.[14]

Thus the chemical shifts of methyl halides vary linearly with concentration in carbon tetrachloride, 2,2-dimethylpropane and carbon disulfide, but not in benzene. For solutions in benzene, the departure from a linear dependence of chemical shift on concentration is approximately the same for the chloride, bromide and iodide. These departures probably are caused by preferred orientations of the benzene ring with respect to the halogen, as mentioned previously. The volume magnetic susceptibilities of carbon tetrachloride, benzene, carbon disulfide, and 2,2-dimethylpropane are -0.693×10^{-6},[14] -0.617×10^{-6},[14] -0.68×10^{-6}[15] and -0.55×10^{-6},[15] respectively. Calculations involving the expression reported by Dickenson[16] and outlined above show that the changes in the chemical shifts of the methyl halides upon dilution in carbon tetrachloride, carbon disulfide and 2,2-dimethylpropane parallel the changes in the bulk diamagnetic susceptibility of the media. For instance, the chemical shift of methyl chloride upon going from 100 to 0% concentrations in carbon tetrachloride was calculated to change by −14.9 cycles and was observed to change by −14.5 cycles. However, the chemical shifts of the methyl halides upon dilution in *benzene* increased much more than predicted from considerations of bulk magnetic susceptibility alone.

The values of the chemical shifts obtained by extrapolation to infinite dilution in the four solvents are plotted against Huggins' electronegativity values in Fig. 3. The lines are straight and almost parallel. Hence while the values of chemical shift at infinite dilution vary with the solvent employed the relative order remains the same and a linear relation of chemical shift and electronegativity is apparent.

Hydrogen NMR Spectra of Ethyl Halides.—Before this research, a correlation of proton chemical shifts had been made by Dailey and Shoolery.[11] The differences between the methyl and methylene proton resonance frequencies of each of the ethyl halides in 50% solution in benzene were measured and were plotted against Huggins' electronegativity values. A linear relation was observed. The statement of this relation implied (a) that the electronegativity of the halogen would affect the electron distribution around the methylene hydrogen atoms, (b) that the electron-withdrawing effect of the halogens would be attenuated in the carbon–carbon bond, and (c) that the effect of bulk diamagnetic susceptibility is the same for methyl and methylene hydrogen nuclei. Dailey and Shoolery also measured the hydrogen NMR spectra of the methyl halides in 50% solution in benzene and observed that the chemical shifts of the methyl halides were proportional to the differences of the methyl and methylene chemical shifts in the corresponding ethyl halides.

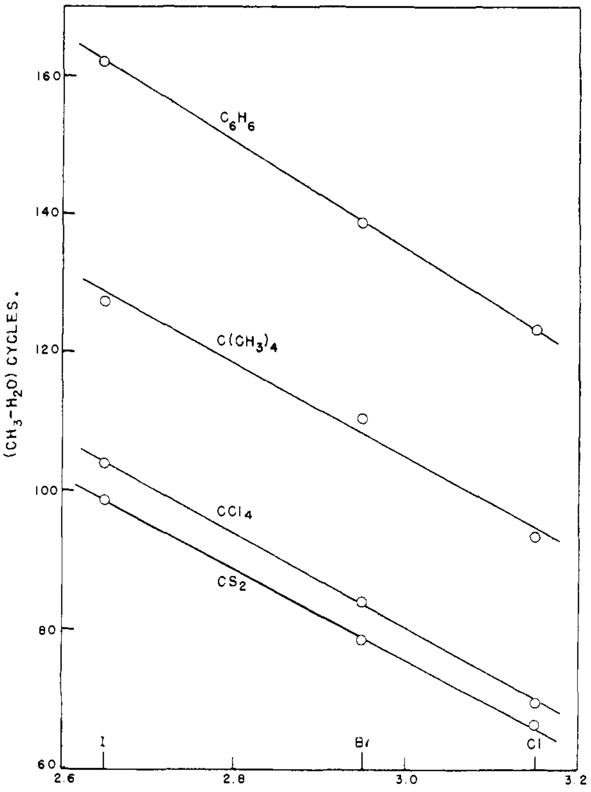

Fig. 3.—Chemical shifts of the methyl halides at infinite dilution in various solvents plotted against electronegativity.

The assumptions inherent in Dailey and Shoolery's approach may be examined in the light of data obtained during this research. To determine whether the electron-withdrawing effect of the halogens is attenuated in the carbon–carbon bond, the chemical shifts of the hydrogen atoms in the *methyl* groups of *ethyl* chloride and *ethyl* bromide were measured in varying concentrations in carbon tetrachloride. The chemical shifts (CH_3-H_2O) in cycles, of these hydrogen atoms *at infinite dilution* in carbon tetrachloride are 129 for ethyl chloride and 122 for ethyl bromide, showing that the electron-withdrawing effect is *not* completely attenuated in the carbon–carbon bond. The data for benzene solutions in Table I give curved-line plots

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(14) C. M. French and V. C. G. Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

(15) Calculated from Pascal's constants: P. Pascal, *Ann. Chim.*, **19**, 5 (1910).

(16) W. C. Dickenson, *Phys. Rev.*, **81**, 717 (1951).

which show that there is association of methyl halides in benzene. As indicated above, the chemical shifts of methyl halides in 100 and 0% solutions of benzene can be calculated on the basis of bulk diamagnetic susceptibility, and comparison with the observed values indicates that the chemical shifts of the hydrogen atoms are influenced by benzene, probably by virtue of its magnetic anisotropy.

Influence of Substituents on the Chemical Shift of an Adjacent Methyl Group.—The chemical shifts of the hydrogen atoms in the methyl groups of twenty-one compounds (not including the methyl derivatives of the halogens) relative to water are recorded in Table II. The observed order is attributed mostly to changes both in electronegativity and in hybridization. In general, for a series of compounds in which the hybridization in the methyl-to-substituent bond remains approximately constant, trends are observed which can be correlated with properties associated with inductive effects. As examples, (a) the chemical shifts of the methyl groups bonded to oxygen are all in the range 19 to 62 cycles, and the chemical shifts of the methyl groups bonded to carbon are all in the range 79 to 154 cycles; (b) the greater chemical shift, indicating more electronic shielding, of dimethyl sulfite than of dimethyl sulfate parallels the lower acid strength of sulfurous acid in comparison with sulfuric acid; and (c) the chemical shifts of acetone and of acetoxime indicate that the electron-withdrawing powers of $>C{=}O$ and $>C{=}NOH$ are approximately equal. It is noted that the changes of hybridization and of the chemical shift of the methyl group in the series formed by toluene, methyl cyanide and tetramethylmethane are comparable with the changes of hybridization and of the chemical shifts (reported by Meyer, Saika and Gutowsky[10]) of the hydrogen atoms in the series formed by ethylene, acetylene and ethane.

Since the hybridization of orbitals forming the methyl–halogen bond varies considerably, in general, from that of the methyl-substituent (other than halogen) bond, the relation shown in Fig. 2 cannot accurately be used to assign effective electronegativity values to all substituent atoms or groups. However, for a series of compounds in which the hybridization of orbitals in the methyl-substituted bond is approximately constant, it may be concluded that the chemical shifts of the compounds in very dilute solutions of carbon tetrachloride should reflect the electronegativity of the substituent.

Meyer, Saika and Gutowsky[10] observed the hydrogen NMR spectra of many of the compounds reported in this section. Their data, obtained mostly for pure compounds, agree well with the corresponding data of this research. Dailey and Shoolery[11] reported the chemical shifts of hydrogen in the methyl and the ethyl derivatives of many of these substituents in 50% solutions of benzene. As mentioned above, they reported the chemical shifts of the ethyl derivatives as the difference of the resonance frequencies of the methyl and methylene groups, but their results show the same qualitative order as ours.

Acknowledgments.—A. L. A. wishes to thank the Natvar Corporation for a generous Fellowship. We are grateful to Dr. Aksel A. Bothner-By and to Dr. M. Kent Wilson for helpful discussions, and to the Esso Education Foundation and the Office of Naval Research for grants in aid.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM SIR JOHN CASS COLLEGE, ALDGATE]

Localization of π-Electrons and the Mechanism of Free Radical Reactions

BY H. H. GREENWOOD[1]

RECEIVED MAY 8, 1957

Simple molecular orbital theory is used to show that a collision process between a conjugated molecule and an attacking reagent in which the C–H bond at the position of attack is displaced out of the plane of the molecule will tend to produce a free electron derived from the π-electron system at the position of attack. This process is suggested as forming part of the mechanism of free radical attack upon conjugated molecules.

It has generally been supposed in the interpretation of the reactions of conjugated molecules with free radicals that the conjugated molecule provides a free electron derived from the π-electron system for bond formation at the position of attack.[2-6] The extent to which this notion may be taken literally is perhaps a matter of opinion, though clearly the formation of a localized σ-type bond C–X in the conventional transition state configuration (Fig. 1) implies a large probability for a spin coupled pair in the region of the bond, one drawn from the π-electron system, the other from the free radical.

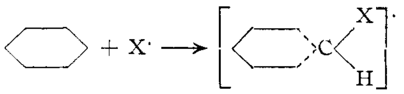

Fig. 1.

One of the difficulties of such an interpretation lies in the phenomenological explanation of the localization of the free electron which is derived from the π-electron system. The usual explanation supposes that the free electron is provided to satisfy the valence requirements of the attacking reagent. One objection to this explanation is that on the one

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(1) Imperial Chemicals Industries Ltd., Billingham Division, Co. Durham, England.

(2) G. W. Wheland, THIS JOURNAL, **69**, 900 (1942).

(3) C. A. Coulson, *Research*, **4**, 307 (1951).

(4) D. H. Hey and G. H. Williams, *Disc. Faraday Soc.*, No. 14, 216 (1953).

(5) W. A. Waters, *ibid.*, No. 14, 247 (1953).

(6) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).