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The Resonance Energies of Certain Organic Free Radicals and Ions[1]

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RECEIVED APRIL 7, 1952

Calculations of π-bond resonance energies using molecular orbital and valence bond methods are made for the following free radicals: allyl, divinyl methyl, trivinyl methyl, cyclopentadienyl and cycloheptatrienyl. The radicals are assumed to be planar with the carbon atoms in the sp^2 state of hybridization, and the calculations are made neglecting orthogonality integrals and overlap integrals of non-adjacent carbon atoms. The results of the two methods are in good agreement with each other for the non-cyclic radicals, but not for the cyclic radicals. The values obtained are (in the order of the above listing of radicals): 18, 30, 39, 38 and 51 kcal./mole. Using these values in conjunction with Franklin's group equivalent method of estimating heat of formation, bond dissociation energies in compounds containing the radicals are calculated. Resonance energies of the positive and negative ions corresponding to the above radicals are calculated by the molecular orbital method.

This paper reports the results of calculations of the resonance energies of the allyl, divinyl methyl, trivinyl methyl, cyclopentadienyl and cycloheptatrienyl free radicals using both the valence bond and LCAO-molecular orbital methods and the molecular orbital method for the corresponding ions. The calculations are made to the usual degree of approximation; that is, in the valence bond method all exchange integrals other than those involving single electron exchanges between adjacent atoms are ignored as are all exchange terms in the overlap integral. Similarly, in the molecular orbital calculations all exchange integrals between non-adjacent carbon atoms are ignored, and the atomic orbitals out of which the molecular orbitals are constructed are considered to be orthonormal. Only the resonance energy of the C–C π-bonds is calculated, and for this purpose it is assumed, as is reasonable, that all the carbon atoms of the radicals and ions are in an sp^2 state of hybridization and that the carbon skeletons are planar. As will be discussed below, the latter assumption introduces some error in the case of the cycloheptatrienyl radical and ion.

The valence bond calculations for allyl, divinyl methyl and trivinyl methyl radicals were made using the phantom electron artifice of Pauling and Wheland[2] and the technique of superposing the graphical representations of the bond eigenfunctions. In the case of the cyclopentadienyl and cycloheptatrienyl radicals the bond eigenfunctions and elements of the secular determinants were obtained by the methods outlined by Eyring, Walter and Kimball.[3] The cycloheptatrienyl radical calculation was made using only the bond eigenfunctions involving bonds between adjacent carbon atoms. These do not constitute a complete set, but it is felt that the resultant error in the energy calculation is small and unimportant. The single exchange integrals in the valence bond and molecular orbital methods were taken to have the values −36 and −20 kcal./mole, respectively. Details of the calculations are summarized in Table III.

The resonance energies are given in Table I.

The trends in the values are as one might expect except for the valence bond values for the two cyclic radicals, and in these cases the agreement with the molecular orbital values is also quite poor. In view of the fact that the lowest roots in these two cases are doubly degenerate, this is not unexpected. Splitting of the degeneracy in higher approximation might occur, thereby lowering the energy of the ground state, or possibly the Jahn–Teller[4] effect might be operative. Thus the resonance energies calculated here are of questionable significance and are not really comparable with those obtained from the molecular orbital method.

TABLE I

RESONANCE ENERGIES OF FREE RADICALS AND IONS

	Resonance energy (kcal./mole)			
	R·			
R	VB	MO	R$^+$	R$^-$
Allyl	18	17	17	17
Divinyl methyl	30	29	29	29
Trivinyl methyl	38	40	40	40
Cyclopentadienyl	27	38	25	50
Cycloheptatrienyl	39	51	60	42

The resonance energies of the allyl and cyclopentadienyl radicals have been calculated by Roberts and Skinner[5] by the molecular orbital method (RE = 19.4 and 37.4 kcal./mole, respectively), and quite recently Roberts, Streitweiser and Regan[6] have published molecular orbital values for cyclopentadienyl and cycloheptatrienyl radicals and carbonium ions (radical $RE = 1.85\,\beta, 2.54\,\beta$; ionic $RE = 1.24\,\beta, 2.99\,\beta$).

In the calculations it was assumed that all of the carbon atoms involved in the resonance structure were coplanar. This seems reasonable for all of the radicals and ions considered except cycloheptatrienyl where the ring is probably slightly puckered. As a consequence the resonance energy will undoubtedly be somewhat smaller than the calculated value. The extent of the reduction is not known, although we have estimated it to be on the order of 5–10 kcal./mole. This estimated reduction, however, has not been included in these calculations.

The value for the allyl radical can be checked from experiment. From Sehon and Szwarc's[7] value of 62 kcal./mole as the energy required to remove a methyl radical from 1-butene and Roberts

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[1] Presented at the Seventh Southwest Regional Meeting of the American Chemical Society, Austin, Texas, December, 1951.

[2] L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

[3] H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 242 ff.

[4] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (*London*), **A161**, 220 (1937).

[5] J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

[6] J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, THIS JOURNAL, **74**, 4579 (1952).

[7] A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A202**, 263 (1950).

and Skinner's[5] value of 32 kcal./mole for the heat of formation of the methyl radical, the heat of formation of the allyl radical can be calculated to be 30 kcal./mole. Using Franklin's[8] method of group equivalents as extended to ions and radicals, the heat of formation of the allyl radical without resonance would be 49 kcal./mole. Thus, the resonance energy is 19 kcal./mole, which is in good agreement with the calculated value.

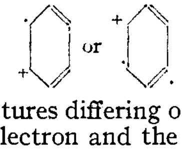
TABLE II

BOND DISSOCIATION ENERGIES (KCAL./MOLE)

Radical	ΔH_f-(R)	D(R-H)	D(R-CH_3)	D(R-C_2H_5)	D(R-Cl)	D(R-R)
$CH_2{=}CH{-}\dot{C}H_2$	30	77	62	60	59	40
$(CH_2{=}CH)_2\dot{C}H$	34	60	47	45	44	10
$(CH_2{=}CH)_3C\cdot$	40	40	36	34	33	(−17)
Cyclopentadienyl	40	63	49	47	46	14
Cycloheptatrienyl	46	54	40	38	37	(−4)

However, with regard to the allyl carbonium ion, the electron impact results of Franklin and Lumpkin[9] seem to indicate no resonance to be present in allyl ion (or benzyl ion, to which the same considerations apply), which disagrees sharply with the calculated value of 17 kcal./mole.

Making further use of the group equivalent method of calculating heats of formation, one can obtain an indication, as follows, that the molecular orbital cyclopentadienyl resonance energy is of the right order of magnitude. The ionization of benzene is considered to involve the removal of one of the carbon π electrons, and the structure of the resulting ion may formally be represented by

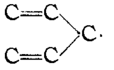
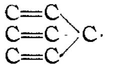
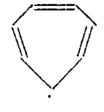


Five similar structures differing only in the position of the unpaired electron and the double bonds can be written, giving a situation analogous to that in the cyclopentadienyl radical. It thus appears reasonable to take the free-electron resonance energy in the benzene ion as identical with that in the cyclopentadienyl radical. The heat of formation of any one of the structures participating in the resonance can be calculated from the group equivalent method; the addition of the free-electron resonance energy gives the heat of formation of the ion. Thus using the molecular orbital resonance energy, $\Delta H_f\ (C_6H_6^+) = 241$ kcal./mole, from which the ionization potential is 221 kcal./mole = 9.6 e.v. The experimental value is 9.24 e.v.[10] A similar calculation for toluene gives an ionization potential of 9.0 e.v., to be compared with the experimental value of 8.92 e.v.[10]

The heat of formation of the radicals with which this work is concerned can be calculated from the group equivalent method and the calculated resonance energies. Then one can easily calculate the dissociation energies of bonds in compounds which will break to give the radicals in question. The following calculation is illustrative

TABLE III

MATRIX ELEMENTS AND ENERGIES

Radical	Valence bond Matrix element,[a] diagonal and above	Valence bond E	Valence bond RE	Molecular orbital E	Molecular orbital RE R·	Molecular orbital RE R^+	Molecular orbital RE R^-
C=C—C·	$D_{11,22} = C + {}^1/_2\alpha$ $D_{12} = {}^1/_2C + \alpha$	$Q \pm \alpha$	${}^1/_2\alpha$	$Q \pm \sqrt{2}\beta$ Q	0.83β	0.83β	0.83β
	$D_{11\ldots33} = C + \alpha$ $D_{12,13} = {}^1/_2C + {}^5/_4\alpha$ $D_{23} = {}^1/_4C + \alpha$	$Q + 1.83\alpha$ Q $Q - 0.83\alpha$	0.83α	$Q \pm \sqrt{3}\beta$ $Q \pm \beta$ Q	1.47β	1.47β	1.47β
	$D_{11\ldots44} = C + {}^3/_2\alpha$ $D_{12,13,14} = {}^1/_2C + {}^3/_2\alpha$ $D_{23,24,34} = {}^1/_4C + {}^9/_8\alpha$	$Q + 2.58\alpha$ $Q + 0.50\alpha$ $Q + 0.50\alpha$ $Q - 0.58\alpha$	1.08α	$Q \pm 2\beta$ $Q \pm \beta$ $Q \pm \beta$ Q	2β	2β	2β
	$D_{11\ldots55} = C + {}^1/_2\alpha$ $D_{12,15,23,34,45} = {}^1/_4Q + {}^1/_2\alpha$ $D_{13,14,24,25,35} = -{}^1/_2Q - \alpha$	$Q + 1.24\alpha$ $Q + 1.24\alpha$ $Q - \alpha$ $Q - 3.24\alpha$ $Q - 3.24\alpha$	0.74α	$Q + 2\beta$ $Q + 0.63\beta$ $Q + 0.63\beta$ $Q - 1.62\beta$ $Q - 1.62\beta$	1.89β	1.26β	2.52β
	$D_{11\ldots77} = C + \alpha$ $D_{12,17,23,34,45,56,67} = -{}^1/_8C - {}^1/_2\alpha$ $D_{13,16,24,27,35,46,57} = -{}^1/_2C - {}^5/_4\alpha$ $D_{14,15,25,26,36,37,47} = {}^1/_4C + \alpha$	$Q + 2.08\alpha$ $Q + 2.08\alpha$ $Q - 0.21\alpha$ $Q - 0.21\alpha$ $Q - 1.41\alpha$ $Q - 1.41\alpha$ $Q - 2\alpha$	1.08α	$Q + 2\beta$ $Q + 1.25\beta$ $Q + 1.25\beta$ $Q - 0.45\beta$ $Q - 0.45\beta$ $Q - 1.8\beta$ $Q - 1.8\beta$	2.55β	3β	2.10β

[a] $C = Q - E$.

$$\Delta H_f[(CH_2{=}CH)_2\overset{H}{C}\cdot] = 2\Delta H_f(CH_2\overset{H}{C}{-}) + \Delta H_f(\overset{|}{\underset{|}{HC}}\cdot) -$$

$$RE = 2 \times 15 + 34 - 30 = 34 \text{ kcal./mole}$$

$$D[(CH_2{=}CH)_2\overset{H}{C}{-}H] = \Delta H_f[(CH_2{=}CH)_2\overset{H}{C}\cdot] + \Delta H_f(H\cdot) -$$

$$\Delta H_f[(CH_2{=}CH)_2CH_2] = 34 + 52 - 26 = 60 \text{ kcal./mole}$$

The bond dissociation energies so calculated are given in Table II. The radical resonance energies are the averages of the MO and VB values except for the cyclic radicals, for which only the MO values are used. Because of lack of data it is necessary to estimate the heats of formation of a number of the compounds by the group equivalent method. In the case of compounds containing the cyclopentadienyl and cycloheptatrienyl rings the amounts of ring strain are assumed to be the same

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[8] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[9] J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951).

[10] W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

as those in cyclopentane and cycloheptane, namely, 6 kcal./mole in both cases. The amounts of double-bond resonance in the rings are estimated by comparing the heats of formation of cyclopentadiene and cycloheptatriene as calculated from the data given in Branch and Calvin[11] with the heats of formation as calculated with the group equivalent method. The values thus obtained are 6 and 14 kcal./mole, respectively. The resonance energy calculated for the cyclopentadienyl and cycloheptatrienyl radicals should be the total resonance energy and no further allowance for double bond resonance has been made.

It is difficult to assess the uncertainty in the calculated dissociation energies, but the authors are of the opinion that ±5 kcal./mole would be a reasonable estimate in all cases except those involving the cycloheptatrienyl radical where the uncertainty is somewhat greater.

BAYTOWN, TEXAS

(11) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice–Hall, New York, N. Y., 1941, pp. 275–279.

[CONTRIBUTION NO. 876 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Electric Moments and Structures of Organosilicon Compounds. II. The Aromatic Carbon–Silicon Bond[1,2]

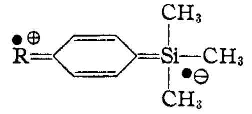
BY HENRY FREISER, MARY V. EAGLE AND JOHN SPEIER

RECEIVED AUGUST 29, 1952

The dielectric constants and densities of benzene solutions of trimethylphenylsilane, trimethyl-*o*-tolylsilane, trimethyl-*m*-tolylsilane, trimethyl-*p*-tolylsilane, *m*-chlorophenyltrimethylsilane, trimethyl-*m*-nitrophenylsilane, chloromethyldimethylphenylsilane, dimethyldiphenylsilane and bis-(chloromethyl)-dimethylsilane have been determined at 30.0°. The dipole moment values of these compounds have been calculated as 0.42, 0.61, 0.50, 0.48, 1.83, 4.28, 1.93, 0.34 and 2.21 *D*, respectively. The results indicate the importance of the so-called "reverse halogen" behavior of silicon and the significance of structures of the type $(CH_3)_3Si^{\oplus}{}^{\ominus}{:}R$. Other structural implications of the results are also discussed.

In paper I, the dipole moments of some aliphatic organosilicon compounds were discussed in terms of the great ease with which the silicon atom can be electrically distorted. In this report, our work was extended to include compounds containing silicon–phenyl linkages. Two previous publications in this area are of considerable interest. Roberts, *et al.*,[3] had reported the dipole moment values of trimethylphenylsilane and some of its *p*-halogenated derivatives. They considered the value of the $(CH_3)_3Si{-}C_{arom}$ group moment obtained from the measurement of $(CH_3)_3SiC_6H_5$, 0.44 *D*, too high due to incorrect evaluation of atomic polarization. Since the value calculated from the *p*-halogenated derivatives was considerably less than 0.44 *D* this was taken as evidence of the undue influence of atomic polarization. Because of the ready distortability of silicon referred to,[1] and the presence of the substituent on the benzene ring in position to exert a maximum influence upon the silicon in the compounds used by Roberts, *et al.*, their conclusions are subject to question.

Since the start of the work described in this report a paper by Soffer and De Vries[4] appeared in which the moments of a large number of aryltrimethylsilanes were reported. Soffer and De Vries pointed out how greatly electron-releasing substituents of the benzene ring in the para position affected the $(CH_3)_3Si{-}C_{arom}$ moment. The results obtained by these workers indicate the great importance of structures of the type



in describing the variation of the $(CH_3)_3Si{-}C_{arom}$ group moment. While Soffer and De Vries suggest that the importance of this structure is limited to R = alkyl, amino and other electron-releasing groups, we feel that in trimethylphenylsilane itself (R = H) the structure also contributes to the description of the ground state. The dipole moments of trimethylphenylsilane, the three isomeric trimethyltolylsilanes although previously reported were examined as were those of *m*-chlorophenyltrimethylsilane, trimethyl-*m*-nitrophenylsilane, chloromethyldimethylphenylsilane, dimethyldiphenylsilane and bis-chloromethyldimethylsilane.

Experimental

Preparation and Purification of Materials.—Trimethylphenylsilane was prepared by adding an equimolar mixture of chlorotrimethylsilane and chlorobenzene to refluxing toluene containing molten sodium and a small amount of excess chlorotrimethylsilane. The addition was at such a rate as to keep the mixture boiling briskly from the heat of reaction. After the addition was complete, acetic acid was added to destroy any traces of sodium that might have remained. The salts were washed from the organic material with water. Distillation in a 13-mm. Podbielniak Heligrid column afforded trimethylphenylsilane, 90% yield, b.p. 170.6° at 738 mm., n^{25}_{D} 1.4872, d^{25}_{4} 0.8632; sp. ref. 0.3332, calcd.[5] sp. ref. 0.3334. Roberts, *et al.*,[3] report b.p. 98–99° at 80 mm., n^{25}_{D} 1.4880, d^{25}_{4} 0.8680.

Tolyltrimethylsilane.—*o*-Chlorotoluene (502.5 g., 3.95 moles) was mixed with trimethylchlorosilane and added slowly to molten sodium (195 g., 8.5 g. atoms) in 400 ml. of boiling toluene containing sufficient trimethylchlorosilane to lower the reflux temperature to 102°. A total of 475 g., 4.4 moles, of the chlorosilane was used. Reaction was very

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[1] Paper I, THIS JOURNAL, **73**, 5229 (1951).

[2] Abstracted from the thesis of M. V. E. submitted in partial fulfillment of the requirements of the M.S. degree in Chemistry, Summer, 1952.

[3] J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

[4] H. Soffer and T. De Vries, *ibid.*, **73**, 5817 (1951).

[5] E. L. Warrick, *ibid.*, **68**, 2455 (1946).