to the partial solubility of the substrate in the aqueous phase.

Experimental Section

NMR spectra were recorded on a Varian EM-390 90-MHz spectrometer in CCl_4 solutions with Me_4Si as internal reference. IR spectra were measured as films on a Perkin-Elmer 377 grating spectrophotometer. GC data were obtained on a PYE Series 104 chromatograph using a 3% SE-30 on Chromosorb column.

The general procedure for the preparation of 2-bromododecane is as follows. A mixture of 16.8 g of 1-docecene (0.1 mol), 55.5 mL of 48% hydrobromic acid (0.5 mol), and 5.1 g of hexadecyltributylphosphonium bromide (0.01 mol) is heated at 115 °C (bath temperature) with magnetic stirring for 2 h. After this time, NMR analysis shows a 94% conversion into 2-bromododecane. The organic layer is separated, the aqueous phase is extracted with dichloromethane, and the solvent is evaporated. The resulting oil is distilled to give 21.4 g (86.0%) of pure 2-bromododecane: bp 125–126 °C (9 mm); $n^{22}{}_D$ 1.4594 [lit.[5] bp 125–130 °C (10 mm); $n^{21}{}_D$ 1.4600]. By treatment of the distillation residue with petroleum ether 4.8 g (94.0%) of phosphonium bromide [mp 52–54 °C (lit.[6] mp 54 °C)] is recovered, which can be reused without further purification.

In the case of lower boiling alkenes, the reactions are carried out at the reflux temperature of the substrate.

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; 1-dodecene, 112-41-4; 1-tetradecene, 1120-36-1; 1-hexadecene, 629-73-2; 2-hexene, 592-43-8; 7-tetradecene, 10374-74-0; 1-bromoundec-10-ene, 7766-50-9; undec-10-en-1-ol, 112-43-6; undec-10-enoic acid, 112-38-9; methylenecyclohexane, 1192-37-6; cyclohexene, 110-83-8; styrene, 100-42-5; (*E*)-stilbene, 103-30-0; (*Z*)-stilbene, 645-49-8; 2-bromohexane, 3377-86-4; 2-chlorooctane, 628-61-5; 2-bromooctane, 557-35-7; 2-iodooctane, 557-36-8; 2-bromododecane, 13187-99-0; 2-bromotetradecane, 74036-95-6; 2-bromohexadecane, 74036-96-7; 7-bromotetradecane, 74036-97-8; 1,10-dibromoundecane, 74036-98-9; 10-bromoundecanoic acid, 18294-93-4; 1-bromo-1-methylcyclohexane, 931-77-1; bromocyclohexane, 108-85-0; 1-chloro-1-phenylethane, 672-65-1; 1-bromo-1-phenylethane, 585-71-7; 1,1-diphenylethylene, 530-48-3; HBr, 10035-10-6; HCl, 7647-01-0; HI, 10034-85-2.

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Optimum HMO Parameters for the Three Models of the Methyl Group[1a]

Cyril Párkányi,* William C. Herndon,* and Ahmad S. Shawali[1b]

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968

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Over the years, hyperconjugation has remained one of the controversial topics in theoretical organic chemistry. Although it has been well established that in many cases the presence or absence of a methyl or other alkyl groups attached to a π-electron system does not significantly alter its physical and chemical properties, there are situations in which the effect of the methyl group clearly manifests itself. Heats of hydrogenation and combustion of alkenes, the red shift of the longest wavelength absorption bands in the electronic absorption spectra of alkenes and methylated aromatic hydrocarbons (in alkenes, the red shift is about 5 nm per methyl group), and the ionization potentials of methylated π-electron hydrocarbons can serve as examples. Hyperconjugation is believed to arise from an overlap of σ bonds in the alkyl substituent with the π system, i.e., with a $2p_z$ orbital of the adjacent carbon atom. Thus, it is obvious that, at least in some cases, it is important to include the methyl group(s) in the calculations when a theoretical treatment of such systems is being carried out.

Chart I

Conjugation Model ($C{-}Y{-}Z = C{-}C{\equiv}H_3$)

$\alpha_C = \alpha - 0.1\beta$ $\beta_{C\text{-}Y} = 0.8\beta$

$\alpha_Y = \alpha$ $\beta_{Y\text{-}Z} = 3.0\beta$

$\alpha_Z = \alpha - 0.5\beta$

Inductive Model

$\alpha_{C(Me)} = \alpha - 0.5\beta$ $\beta_{C\text{-}Me} = 0$

Heteroatom Model

$\alpha_{C(Me)} = \alpha - 0.2\beta$ $\beta_{C\text{-}Me} = 0.7\beta$

$\alpha_{Me} = \alpha + 2.0\beta$

At present, there are three models of the methyl group available within the framework of the simple HMO method. In the conjugation (or hyperconjugation) model, the methyl group is approximated as a modified attached vinyl group, C–Y–Z, where C is the π-network carbon atom to which the methyl group is attached, Y is the sp^3-hybridized carbon atom of the methyl group, and Z represents the three hydrogen atoms of the methyl group considered together as a pseudoatom ($CYZ = CC{\equiv}H_3$). In this model, the sp^3 carbon atom of the methyl group contributes one electron into the delocalized π system as well as do the three hydrogen atoms together.[2-4]

Another simple model of the methyl group, which is called the inductive model and is due to Wheland and Pauling[5] and Longuet-Higgins,[6,7] neglects any possible conjugation between the methyl group and the π system and considers only its inductive effect alone. In this model, the methyl group itself does not explicitly appear in the calculation, and its effect is reflected in the modified value of the Coulomb integral of the carbon atom to which it is attached. Finally, in the heteroatom model of the methyl group, the methyl group is taken as a pseudoheteroatom, Me, representing a π-electron center and contributing a pair of electrons to the π system.[8,9] The heteroatom model of the methyl group was also used in the PPP method.[10,11]

The parameters suggested for the three models of the methyl group have been summarized by Streitwieser[12] as shown in Chart I (α_X and β_{XY} are the Coulomb and resonance integrals, respectively).

Although the above parameters have been widely employed,[13-21] no parameter study has been carried out to

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Table I. Ionization Potentials of Methyl-Substituted Ethylenes, Butadienes, and Benzenes (Heteroatom Model)[a]

compd	exptl (calcd) ionization potential			ref (exptl)
	I_1	I_2	I_3	
	Ethylenes			
ethylene	10.50 (10.52)			27
propene	9.91 (9.87)			27
cis-2-butene	9.32 (9.22)			27
trans-2-butene	9.12 (9.22)			27
2-methyl-2-butene	8.68 (8.74)			28
2,3-dimethyl-2-butene	8.27 (8.24)			28
	Butadienes			
1,3-butadiene	9.03 (8.99)	11.46 (11.30)		29
1,3-pentadiene	8.61 (8.59)	11.10 (11.11)		29
2-methyl-1,3-butadiene (isoprene)	8.89 (8.80)	11.10 (10.75)		29
2,4-hexadiene	8.09 (8.18)	10.60 (10.87)		30
trans-2,3-dimethyl-1,3-butadiene	8.62 (8.69)	10.18 (10.18)		29
2-methyl-1,3-pentadiene	8.47 (8.69)	10.50 (10.49)		30
4-methyl-1,3-pentadiene	8.28 (8.34)	10.80 (11.02)		29
3-methyl-1,3-pentadiene	8.39 (8.28)	10.60 (10.64)		30
1,4-dimethyl-2,4-hexadiene	7.83	10.10		29
	Benzenes			
benzene	9.24 (9.06)	9.24 (9.06)	12.25 (12.19)	31
toluene	8.78 (8.68)	9.00 (9.06)	11.30 (11.49)	32
o-xylene	8.45 (8.48)	8.90 (8.88)	11.00 (11.26)	32
m-xylene	8.50 (8.55)	9.00 (8.85)	11.00 (11.08)	32
p-xylene	8.40 (8.38)	9.05 (9.06)	11.10 (10.98)	32
mesitylene (1,3,5-trimethylbenzene)	8.35 (8.55)	8.35 (8.55)	11.00 (10.67)	30
pseudocumene (1,2,4-trimethylbenzene)	8.20 (8.26)	8.80 (8.82)	10.80 (10.77)	30

[a] Different parameters used for each different group of compounds. See the text. The ionization potentials are given in eV.

Table II. Parameters for the Conjugation Model of the Methyl Group[a, b]

	α_Z	β_{C-Y}	β_{Y-Z}
initial	$\alpha - 0.5\beta$	β	3.0β
final (α = 6.95 eV, β = 2.50 eV)	$\alpha - 2.3\beta$	β	3.1β

[a] $C—C{\equiv}H_3$ = C—Y—Z. Values obtained for methylbutadienes and methylbenzenes treated as a single group. [b] α_C and α_Y were α in each case.

Table III. Parameters[a] for the Inductive Model of the Methyl Group

	$\alpha_{C(Me)}$	$\alpha_{C(Me_2)}$
initial	$\alpha - 0.5\beta$	$\alpha - 0.75\beta$
final (α = 6.70 eV, β = 2.44 eV)		
butadienes	$\alpha - 0.6\beta$	$\alpha - 1.10\beta$
benzenes	$\alpha - 0.6\beta$	

[a] β_{C-Me} was zero in each case.

Table IV. Parameters[a] for the Heteroatom Model of the Methyl Group

	α_{Me}	β_{C-Me}
initial	$\alpha + 2.0\beta$	0.7β
final		
ethylenes (α = 6.80 eV, β = 3.70 eV)	$\alpha + 2.57\beta$	0.82β
butadienes (α = 7.56 eV, β = 2.31 eV)	$\alpha + 3.13\beta$	1.22β
benzenes (α = 5.93 eV, β = 3.13 eV)	$\alpha + 1.83\beta$	0.60β

[a] $\alpha_{C(Me)}$ was α in each case.

determine the best possible sets of parameters for the three models of the methyl group. The goal of the present work was to obtain optimum sets of parameters for the above three models. Vertical ionization potentials of π-electron hydrocarbons taken from their photoelectron spectra were used as the experimental basis for the determination of parameters, utilizing the well-known relationship between the calculated energies of occupied π molecular orbitals and experimental ionization potentials.[16,17,21-26]

The HMO calculations were carried out on an IBM 360/65 computer. A generally applicable, least-squares method developed to optimize the parameters of an effective Hamiltonian matrix in any basis set[26] was utilized to find the optimum sets of parameters for the three models of the methyl group, with vertical ionization potentials as the respective experimental quantity. Essentially, this method uses first-order perturbation theory to write simultaneous linear equations relating ionization potentials to unknown matrix elements, and a standard regression analysis gives the parameters. Initial sets of

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Table V. Results of Statistical Analysis of Experimental and Calculated Ionization Potentials[a]

model	compd	I	a	b	n	s	r
conjugation	butadienes + benzenes	I_1	0.828	1.451	15	0.427	0.588
		I_2	0.739	2.665	15	0.306	0.929
		I_3	0.732	3.041	7	0.208	0.881
inductive	butadienes	I_1	1.101	0.875	8	0.114	0.968
		I_2	0.462	5.751	8	0.159	0.831
	benzenes	I_1	0.954	0.339	7	0.129	0.942
		I_2	0.743	2.339	7	0.093	0.926
		I_3	0.408	6.636	7	0.135	0.848
heteroatom	ethylenes	I_1	0.992	0.075	6	0.082	0.996
	butadienes	I_1	0.869	1.117	8	0.066	0.975
		I_2	0.760	2.491	8	0.019	0.874
	benzenes	I_1	0.709	2.498	7	0.075	0.964
		I_2	0.617	3.402	7	0.079	0.923
		I_3	0.986	0.156	7	0.022	0.923

[a] Least-squares method. $I_{\mathrm{exp}}\,(\mathrm{eV}) = aI_{\mathrm{calcd}}\,(\mathrm{eV}) + b$. The other parameters are defined as follows: a, slope; b, intercept; n, number of points; s, standard error; r, correlation coefficient. With the exception of the first correlation (first line), all other data are significant on a 1% probability level.

eigenvector coefficients are obtained upon the choice of an initial set of parameters, and the final parameters are found after iteration to a self-consistent solution.

Table I summarizes the values of ionization potentials of various methyl-substituted ethylenes, butadienes, and benzenes and the respective literature sources as well as the calculated values obtained in the present study. The results of the calculations for the conjugation, inductive, and heteroatom models of the methyl group are given in Tables II–IV, respectively. In all cases, the final parameter values are those obtained after 20 iterations. The Coulomb integrals reflect the electron-donating character of the methyl group and its inductive effect, and the resonance integrals reflect its conjugative ability.[33]

The data obtained for the conjugation model (Table II) indicate that, instead of the hitherto accepted Coulomb integral for the H_3 pseudoatom, $\alpha_Z = \alpha - 0.5\beta$, a value of $\alpha - 2.3\beta$ should be used. The value of the resonance integral between the carbon atom and the H_3 pseudoatom of the methyl group remains almost unchanged, $\beta_{YZ} = 3.1\beta$, as compared to the originally suggested value, $\beta_{YZ} = 3.0\beta$. Statistical analysis of the results using the least-squares method for the regression line between experimental and calculated ionization potentials shows a poor correlation for the first ionization potentials but a very satisfactory correlation for the second and third ionization potentials (Table V). In the case of the inductive model, a satisfactory correlation is obtained both for methylated butadienes and for methylbenzenes (Table V). The optimum value of the Coulomb integral seems to be $\alpha_{\mathrm{C(Me)}} = \alpha - 0.6\beta$ rather than the originally proposed $\alpha_{\mathrm{C(Me)}} = \alpha - 0.5\beta$ (Table III).

The optimum values of the Coulomb and resonance integrals for the heteroatom model vary, depending on the structural type of the compounds studied (Table IV). This point should be emphasized and considered by anyone who wishes to calculate properties by using these parameters. Attempts to treat the individual groups of hydrocarbons (ethylenes, butadienes, benzenes) as a single group or to combine two groups into one lead to much poorer correlations and thus are generally unacceptable. However, our results and our previous experience indicate that the heteroatom model is the best generally applicable model of the methyl group. This can be seen from a comparison of the calculated and experimental ionization potentials summarized in Table I. We recommend the use of the heteroatom model and these parameters in future applications of this type.

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Synthetic Methods and Reactions. 85.[1] Reduction of α-Halo Ketones with Sodium Iodide/Chlorotrimethylsilane

George A. Olah,* Massoud Arvanaghi, and
Yashwant D. Vankar

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90007

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Recently we reported[2] the reduction of α-halo ketones to their parent ketones by using sodium iodide and trimethyl(ethyl)amine–sulfur dioxide or pyridine–sulfur trioxide complexes in acetonitrile solution. Although open-chain aliphatic α-halo ketones were reduced at room temperature by using either of these reagents, α-halocycloalkanones needed prolonged heating to effect the reduction. We, therefore, were interested in finding other reagents, effective under less severe conditions and with shorter reaction times. We report now that, indeed, such a reagent has been found in chlorotrimethylsilane/sodium iodide in acetonitrile solution, which meets the above requirements and can be employed effectively for the reduction of both α-haloalkanones as well as α-halocycloalkanones (see Table I). Although there are several methods[2-4] available to bring about such conversions, we consider the present method a useful addition to them. Chlorotrimethylsilane/sodium iodide is readily available, is inexpensive, and gives excellent yields in simple and easy to carry out reactions under mild conditions.

In general, α-halogenated aliphatic ketones, upon treatment with sodium iodide and chlorotrimethylsilane in acetonitrile solution at room temperature, yield the corresponding parent ketones in 80–94% yield in 3–5 h. α-Halogenated cycloalkanones are reduced, however, at room temperature in the presence of excess of sodium iodide, and ketones are obtained in 75–98% yield in 8–12 h. 2-Chlorocyclopentanone and 2-chlorocyclohexanone are exceptions and require more time (ca. 48 h). The mechanism of the reduction may be represented as in Scheme I.

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