Molecular Orbital Theory of the Electronic Structure of Organic Compounds. V. Molecular Theory of Bond Separation

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Abstract: The complete hydrogenation of an organic molecule is separated into two processes. In the first, termed *bond separation*, the molecule is separated into its simplest parents containing the same component bonds. The energy associated with such a reaction is then the *heat of bond separation*. The second step consists of full hydrogenation of the products of bond separation. To study these two processes, we have performed *ab initio* molecular orbital calculations on a variety of polyatomic molecules. Both minimal and extended basis sets, taken as linear combinations of Gaussian-type functions, are shown to give heats of bond separation in good agreement with experiment. In contrast, only the extended basis is successful in reproducing the heats of hydrogenation of the parents.

An important objective of quantum chemistry is the quantitative estimation of relative stabilities of organic molecules. This goal has often seemed remote because simple treatments, such as single-determinant molecular orbital theory, neglect large effects due to electron correlation and it is therefore extremely difficult to estimate total energies to high accuracy. It has long been recognized that single-determinant molecular orbital theory underestimates the dissociation energies of diatomic molecules for this reason. Recognizing the difficulty of making absolute calculations of total molecular energies, some authors have more modestly attempted a direct calculation of heats of reaction involving closed shell species, where there is some prospect of cancellation of correlation corrections. Recent work by Snyder and Basch[1,2] has shown that heats of complete hydrogenation for a set of molecules containing two or three heavy atoms (C, N, O, or F) are given correctly to within about 30 kcal/mol by single-determinant molecular orbital theory using a Gaussian-type basis set of modest size. This development is encouraging, since the energies of the products of such hydrogenation (methane, ammonia, water, and hydrogen fluoride) are well known experimentally, so that a reliable prediction of the heat of hydrogenation is sufficient to estimate the total energy of the original compound.

For a wide range of organic molecules, it is useful to separate the process of complete hydrogenation into two steps. If we are dealing with a molecule which can be represented by a classical valence structure (without formal charges or unpaired electrons), we may consider, as a first step, the reaction in which all formal bonds between heavy (nonhydrogen) atoms are separated into the simplest (or parent) molecules with this same type of bond. If we restrict ourselves to molecules containing only H, C, N, O, and F, this set of parent molecules consists of ethane, ethylene, acetylene, methylamine, formaldimine, hydrogen cyanide, methanol, formaldehyde, fluoromethane, hydrazine, diimide, hydroxylamine, nitroxyl, fluoramine, hydrogen peroxide, and hypofluorous acid. For stoichiometric balance, an appropriate number of the simple hydrides methane, ammonia, and water must be added to the left-hand side (reactants). Taking methylketene as an example, this reaction would be

$$CH_3{-}CH{=}C{=}O + 2CH_4 \longrightarrow C_2H_6 + C_2H_4 + H_2CO \quad (1)$$

Since all bonds between heavy atoms are separated from one another, this reaction will be termed the *bond separation reaction* and the corresponding heat will be the *heat of bond separation*.

The second step can be formulated as the full hydrogenation of the products of the bond separation reaction. For the example quoted above, the three additional reactions

$$\begin{aligned} C_2H_6 + H_2 &\longrightarrow 2CH_4 \\ C_2H_4 + 2H_2 &\longrightarrow 2CH_4 \\ H_2CO + 2H_2 &\longrightarrow CH_4 + H_2O \end{aligned} \quad (2)$$

are required. Addition of the reactions 1 and 2 then gives the complete hydrogenation reaction

$$CH_3{-}CH{=}C{=}O + 5H_2 \longrightarrow 3CH_4 + H_2O \quad (3)$$

Bond separation reactions such as (1) are examples of chemical changes in which there is retention of the number of bonds of a given formal type, but with a change in their relation to one another. Such processes in general may be termed *isodesmic*. The hydrogenation reactions (eq 2 and 3) are not isodesmic.

Many qualitative and empirical approaches to stability attempt to separate energy contributions which are associated with isodesmic processes. For example, conjugation and resonance in molecules such as 1,3-butadiene and benzene refer to stabilization of extended systems of formal single and multiple bonds when compared with corresponding isolated bonds. Another example is the strain energy of cycloalkanes, which compares single bonds in ring systems with those in open chains. In general, the energies of isodesmic reactions measure deviations from the additivity of bond energies.

It is important to note that a satisfactory method of predicting heats of bond separation would be sufficient to predict the total energy of the molecule, provided that the energies of the bond separation prod-

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(1) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, **91**, 2189 (1969).

(2) L. C. Snyder, *J. Chem. Phys.*, **46**, 3602 (1967).

ucts are known, either experimentally or by fuller theoretical studies.

The main aim of this paper is to test how well heats of bond separation can be calculated using simple molecular orbital methods. This is a reasonable objective since it may be hoped that errors in the description of individual bonds will largely cancel and that smaller interactions between bonds may be handled satisfactorily by relatively simple methods. It will be shown that all methods considered predict heats of bond separation more effectively than heats of hydrogenation of the products of bond separation.

Quantum Mechanical Methods

We shall study a series of closed shell molecules using a single-determinant wave function built from doubly occupied molecular orbitals ψ_i which are constructed in the linear combination of atomic orbital (LCAO) approximation

$$\psi_i = \sum_{\mu} c_{\mu i}\phi_\mu \tag{4}$$

The LCAO coefficients $c_{\mu i}$ are found by solution of the Roothaan equations[3] which then lead to a calculated total energy, given the coordinates and charges of the nuclei.

Three basis sets ϕ_μ will be considered. The first two are minimal sets, consisting of a single function for hydrogen (1s) and five functions for each heavy atom (1s, 2s, 2p). The third is a more flexible extended set in which each valence atomic orbital (1s for H and 2s and 2p for heavy atoms) is replaced by two parts, so that there are two ϕ functions per hydrogen and nine per heavy atom. All ϕ_μ are themselves sums of Gaussian functions chosen as follows.

Basis Set 1 (STO-3G). The first basis set is one which closely simulates a minimal basis of Slater-type (exponential) orbitals. Each ϕ_μ is obtained by rescaling a three-Gaussian least-squares representation of the standard type Slater-type orbital with $\zeta = 1$. Thus

$$\phi_\mu(\zeta,\mathbf{r}) = \zeta^{3/2}\phi_\mu'(\zeta\mathbf{r}) \tag{5}$$

where the ϕ_μ' are ($N = 3$)

$$\begin{aligned}
\phi_{1s}'(\mathbf{r}) &= \sum_{k=1}^{N} d_{1s,k}\, g_{1s}(\alpha_{1k},\mathbf{r}) \\
\phi_{2s}'(\mathbf{r}) &= \sum_{k=1}^{N} d_{2s,k}\, g_{1s}(\alpha_{2k},\mathbf{r}) \\
\phi_{2p}'(\mathbf{r}) &= \sum_{k=1}^{N} d_{2p,k}\, g_{2p}(\alpha_{2k},\mathbf{r})
\end{aligned} \tag{6}$$

g_{1s} and g_{2p} being normalized Gaussian orbitals. The d coefficients and α exponents in (6) are specified elsewhere,[4] together with a standard set of molecular ζ values which are used in this paper.

The STO-3G basis has the merit of great simplicity so that it can be readily applied to quite large molecules without excessive computation. It has already been used to make extensive studies of charge distribution[5] and molecular geometry.[6]

Basis Set 2 (LEMAO-6G). The second set ϕ_μ is one which is designed to give total energies which approach the limit of that which is possible with an isotropic minimal basis. The atomic orbitals ϕ_μ' are again given by sums of the type (6) (with $N = 6$), but the d and α values are now chosen to minimize the calculated energy of the isolated atom. These orbitals are referred to as least energy minimal atomic orbitals (LEMAO) and are specified in full elsewhere,[7] and the ζ scaling parameters for the valence shells are treated as additional variational parameters in the molecular calculations to allow for changes in atomic size depending on the molecular environment. Further details of the minimization procedure and detailed ζ values are given in the Appendix.

We have tested the LEMAO-6G set to find whether heats of bond separation or heats of hydrogenation can be calculated using an isotropic minimal basis or whether an extended basis is essential. The LEMAO-6G calculations are, of course, substantially more time consuming than the STO-3G ones, particularly if scale factor optimization is involved.

Basis Set 3 (4-31G). The third basis is an extended set, containing more than the minimal number of ϕ functions. The inner shell of a heavy atom is still represented by a single function which is a sum of four Gaussians. However, the valence shells (hydrogen 1s and heavy atom 2s and 2p) are described by inner and outer parts which are, respectively, sums of three and one Gaussian functions. As with the minimal sets, Gaussian exponents are shared between 2s and 2p.

The parameters for this basis are determined in a manner similar to the LEMAO set. The coefficients and exponents in expansions such as (6) are first chosen to minimize the energy of the atomic ground states. Scaling factors are then introduced for both parts of the valence functions and varied independently to minimize the energy of a small number of simple molecules. Finally, on the basis of this experience, a set of standard scaling factors is selected and this is used for all calculations reported in this paper. Detailed numerical values are given elsewhere.[8]

Extended bases have been widely used in molecular orbital calculations on small molecules. The reaction heat studies of Snyder and Basch[1,2] are based on a rather larger extended set containing more Gaussian functions. It is to be expected that these extended sets will have certain advantages over minimal sets. In particular, since each valence atomic orbital is split into inner and outer parts, some flexibility of effective atomic size is permitted by variation of the weighting coefficients. Further, this relative inner–outer weighting may be different for different directions, so that anisotropic effects can be taken into account in a way which is not possible with a rescaled isotropic minimal basis. The 4-31G set is designed to take advantage of these flexible features while remaining simple enough to be applied to moderately large molecules.

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[3] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[4] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[5] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2191 (1970).

[6] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

[7] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 5001 (1970).

[8] R. Ditchfield, W. J. Hehre, and J. A. Pople, *ibid.*, in press.

Table I. Calculated and Experimental Energy Data

Molecule	Total energy, hartrees			Zero-point vibrational energy,[bb] hartrees	$\Delta H_f{}^\circ{}_0$,[jj] kcal mol^{-1}
	STO-3G	LEMAO-6G	4-31G		
Hydrogen[a]	−1.11669	−1.12807	−1.12673	0.01004[cc]	0.0
Hydrogen fluoride[b]	−98.57078	−100.01668	−99.88726	0.00943[cc]	−64.789
Water[c]	−74.96293	−75.99017	−75.90739	0.02052	−57.102
Ammonia[d]	−55.45400	−56.14950	−56.10247	0.03287	−9.34
Methane[e]	−39.72653	−40.17468	−40.13938	0.04320	−15.970[kk]
Ethane[f]	−78.30603	−79.17104	−79.11562	0.07214	−16.523[kk]
Methylamine[g]	−94.03043	−95.13420	−95.06888	0.06243	−1.91[ll]
Methanol[h]	−113.54502	−114.96508	−114.86925	0.04961	−45.355
Fluoromethane[i]	−137.16836	−138.99086	−138.85662	0.03817	−54.079[cc]
Ethylene[j]	−77.07232	−77.96240	−77.92103	0.04923	14.515[kk]
Formaldehyde[k]	−112.35375	−113.74949	−113.69209	0.02567	−27.1
Acetylene[l]	−75.85208	−76.76284	−76.71059	0.02579	54.324[kk]
Hydrogen cyanide[m]	−91.67515	−92.76814	−92.73118	0.01557	32.39
Propane[n]	−116.88580	−118.17025	−118.09345	0.09963	−19.482[kk]
Propene[o]	−115.65828	−116.96683	−116.90381	0.07738[dd]	8.468[kk]
Propyne[m]	−114.44397	−115.77078	−115.69964	0.05389	46.017[kk]
Allene[p]	−114.41715	−115.74607	−115.69540	0.05320[dd]	47.70[kk]
Cyclopropane[q]	−115.66147	−116.94739	−116.88029	0.07879	16.79[ll,mm]
Cyclopropene[r]	−114.39944	−115.69476	−115.64172	0.05449[ee]	68.68[ll,mm]
Benzene[s]	−227.89059	−230.47734		0.09748	24[kk]
Difluoromethane[t]	−234.62559	−237.81761	−237.59189	0.03207[ff]	−104.97
Tetrafluoromethane[u]	−429.56857	−435.47116	−435.07291	0.01714	−219.6
Dimethyl ether[v]	−152.13072	−153.94333	−153.83633	0.07736	−39.745
Acetaldehyde[w]	−150.94456	−152.77044	−152.68631	0.05298[gg]	−37.14
Ketene[x]	−149.72440	−151.56247	−151.49411	0.03057[dd]	−13.86
Carbon dioxide[y]	−185.06465	−187.42218	−187.32796	0.01155[dd]	−93.963
Dimethylamine[z]	−132.61078	−134.12003	−134.03708	0.08941[hh]	0.83[ll]
Acetonitrile[m]	−130.27031	−131.78515	−131.72660	0.04393	22.58
Formamide[aa]	−166.67760	−168.76699	−168.67320	0.04665[ii]	−41.72[ll,mm]

[a] References *a–aa* pertain to choice of molecular geometry. B. P. Stoicheff, *Can. J. Phys.*, **35,** 730 (1957).
[b] G. A. Kuipers, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **25,** 275 (1956).
[c] W. S. Benedict, N. Gailar, and E. K. Plyler, *ibid.*, **24,** 1139 (1956).
[d] W. S. Benedict, and E. K. Plyler, *Can. J. Phys.*, **35,** 1235 (1957).
[e] H. C. Allen, Jr. and E. K. Plyler, *J. Chem. Phys.*, **26,** 972 (1957).
[f] D. W. Lepard, D. M. C. Sweeney, and H. L. Welsh, *Can. J. Phys.*, **40,** 1567 (1962).
[g] D. R. Lide, Jr., *J. Chem. Phys.*, **27,** 343 (1957).
[h] E. V. Ivash and D. M. Dennison, *ibid.*, **21,** 1804 (1953).
[i] W. F. Edgell and L. Parts, *J. Amer. Chem. Soc.*, **78,** 2358 (1956).
[j] H. C. Allen, Jr., and E. K. Plyler, *ibid.*, **80,** 2673 (1958).
[k] K. Takagi and T. Oka, *J. Phys. Soc. Jap.*, **18,** 1174 (1963).
[l] J. Callomon and B. P. Stoicheff, *Can. J. Phys.*, **35,** 373 (1957).
[m] C. C. Costain, *J. Chem. Phys.*, **29,** 864 (1958).
[n] D. R. Lide, Jr., *ibid.*, **33,** 1514 (1960).
[o] D. R. Lide, Jr., and D. Christensen, *ibid.*, **35,** 1374 (1961).
[p] A. G. Maki and R. A. Toth, *J. Mol. Spectrosc.*, **17,** 136 (1965).
[q] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17,** 538 (1964).
[r] P. H. Kasai, R. J. Myers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30,** 512 (1959).
[s] A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **34,** 350 (1956).
[t] D. R. Lide, Jr., *J. Amer. Chem. Soc.*, **74,** 3548 (1952).
[u] C. W. W. Hoffmann and R. C. Lidingstone, *J. Chem. Phys.*, **21,** 565 (1953).
[v] U. Blukis, P. H. Kasai, and R. J. Myers, *ibid.*, **38,** 2753 (1963).
[w] R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, 26, 1695 (1957).
[x] A. P. Cox, L. F. Thomas, and J. Sheridan, *Spectrochim. Acta*, **15,** 542 (1959).
[y] C. P. Courtoy, *Ann. Soc. Sci. Bruxelles*, 73, 5 (1959).
[z] J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48,** 5058 (1968).
[aa] R. J. Kurland and E. B. Wilson, Jr., *ibid.*, **27,** 585 (1957).
[bb] Unless otherwise noted, from T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," NSRDS-NBS 6, 11, 17, U. S. Government Printing Office, Washington, D. C.
[cc] "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Company, Midland, Mich., 1965.
[dd] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966.
[ee] D. F. Eggers, J. W. Schultz, K. B. Wiberg, E. L. Wagner, L. M. Jackman, and R. L. Erskine, *J. Chem. Phys.*, **47,** 946 (1967).
[ff] E. K. Plyler and W. S. Benedict, *J. Res. Nat. Bur. Stand.*, **47,** 202 (1951).
[gg] J. C. Evans and H. J. Bernstein, *Can. J. Chem.*, **34,** 1083 (1956).
[hh] G. Dellepiane and G. Zerbi, *J. Chem. Phys.*, **48,** 3573 (1968).
[ii] J. C. Evans, *ibid.*, **22,** 1228 (1954).
[jj] Unless otherwise noted, from D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, W. M. Bailey, and R. H. Schumm, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Technical Note No. 270-3, U. S. Government Printing Office, Washington, D. C.
[kk] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
[ll] Calculated from $\Delta H_f{}^\circ{}_{298}$ and fundamental vibrational frequencies as described in text. Additional references refer to experimental values of $\Delta H_f{}^\circ{}_{298}$.
[mm] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 69, 279 (1969).

Results and Discussion

The three theoretical methods described in the previous section have been applied to the set of molecules listed in Table I. This table lists the total energies calculated for configurations in which the nuclei are fixed in the experimentally determined equilibrium configurations. Also given are energies of zero-point vibration (calculated as $^1/_2h\Sigma_i\nu_i$, where ν_i are experimental vibration frequencies) and observed heats of formation at 0°K. In some cases, it was necessary to estimate heats at 0°K from observed values at $T = 298\,°\mathrm{K}$ using the formulas

$$H_{\mathrm{trans}}(T) = (5/2)RT$$

$$H_{\mathrm{rot}}(T) = RT\ \text{(linear molecule)}$$

$$= (3/2)RT\ \text{(nonlinear molecule)}$$

$$\Delta H_{\mathrm{vib}}(T) = H_{\mathrm{vib}}(T) - H_{\mathrm{vib}}(0) = N\sum_i h\nu_i/(e^{h\nu_i/kT} - 1)$$

In their earlier study, Snyder and Basch[1,2] applied corrections to theoretical energies in order to compare heats of reaction at 298°K with experimental values. We, on the other hand, have applied the vibrational correction to the heat of reaction in order to obtain a reaction energy (at 0°K) for fixed nuclei. This experi-

Table II. Bond Separation Energies

Molecule	Bond separation reaction	Bond separation energy, kcal mol^{-1}: STO-3G	LEMAO-6G	4-31G	Exptl[a]
Propane	$CH_3CH_2CH_3 + CH_4 \rightarrow 2CH_3CH_3$	0.2	1.8	1.0	1.5 (2.4)
Propene	$CH_3CHCH_2 + CH_4 \rightarrow CH_3CH_3 + CH_2CH_2$	4.1	5.1	4.0	5.0 (5.5)
Propyne	$CH_3CCH + CH_4 \rightarrow CH_3CH_3 + CHCH$	7.8	7.3	8.0	7.2 (7.8)
Allene	$CH_2CCH_2 + CH_4 \rightarrow 2CH_2CH_2$	−0.6	−2.5	−4.6	−4.1 (−2.7)
Cyclopropane	$\overline{\mathrm{CH_2CH_2C}}\mathrm{H_2} + 3CH_4 \rightarrow 3CH_3CH_3$	−48.3	−26.2	−30.4	−23.5 (−18.5)
Cyclopropene	$\overline{\mathrm{CH_2CHC}}\mathrm{H} + 3CH_4 \rightarrow 2CH_3CH_3 + CH_2CH_2$	−66.1	−53.8	−58.0	−45.2 (−39.3)
Benzene	$C_6H_6 + 6CH_4 \rightarrow 3CH_3CH_3 + 3CH_2CH_2$	72.0	78.5		61.1 (65.8)
Difluoromethane	$CH_2F_2 + CH_4 \rightarrow 2CH_3F$	9.7	6.6	11.3	12.1 (12.8)
Tetrafluoromethane	$CF_4 + 3CH_4 \rightarrow 4CH_3F$	45.2	19.9	40.5	47.5 (51.2)
Dimethyl ether	$CH_3OCH_3 + H_2O \rightarrow 2CH_3OH$	2.3	2.1	3.3	5.3 (6.1)
Acetaldehyde	$CH_3CHO + CH_4 \rightarrow CH_3CH_3 + H_2CO$	7.1	15.4	11.3	8.5 (9.5)
Ketene	$H_2CCO + CH_4 \rightarrow CH_2CH_2 + H_2CO$	15.6	15.9	12.8	16.5 (17.3)
Carbon dioxide	$OCO + CH_4 \rightarrow 2H_2CO$	52.5	61.4	52.2	57.9 (55.7)
Dimethylamine	$CH_3NHCH_3 + NH_3 \rightarrow 2CH_3NH_2$	2.5	0.7	1.1	3.1 (4.7)
Acetonitrile	$CH_3CN + CH_4 \rightarrow CH_3CH_3 + HCN$	9.8	13.0	12.0	8.9 (9.3)
Formamide	$NH_2CHO + CH_4 \rightarrow CH_3NH_2 + H_2CO$	12.5	36.4	32.4	29.8 (28.7)

[a] Heats of reaction at 0°K corrected for zero-point vibration. Uncorrected heats are given in parentheses.

Table III. Hydrogenation Energies of Products of Bond Separation Reactions

Hydrogenation reaction	Calculated: STO-3G	LEMAO-6G	4-31G	Experimental[a]
$CH_3CH_3 + H_2 \rightarrow 2CH_4$	−19.0	−31.5	−22.9	−18.1 (−15.4)
$CH_3NH_2 + H_2 \rightarrow CH_4 + NH_3$	−21.0	−38.8	−29.0	−25.7 (−23.4)
$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−17.4	−45.0	−31.9	−30.3 (−27.7)
$CH_3F + H_2 \rightarrow CH_4 + HF$	−7.7	−45.5	−27.2	−29.5 (−26.7)
$CH_2CH_2 + 2H_2 \rightarrow 2CH_4$	−92.5	−82.1	−65.4	−57.2 (−46.5)
$H_2CO + 2H_2 \rightarrow CH_4 + H_2O$	−64.2	−99.9	−63.5	−57.3 (−46.0)
$CHCH + 3H_2 \rightarrow 2CH_4$	−157.5	−127.0	−118.0	−105.4 (−86.3)
$HCN + 3H_2 \rightarrow CH_4 + NH_3$	−97.5	−107.8	−81.9	−76.8 (−57.7)

[a] Heats of reaction at 0°K corrected for zero-point vibration. Uncorrected heats are given in parentheses.

mentally derived quantity may then be compared directly with the three purely theoretical *ab initio* energies. Table II gives the bond separations for the molecules containing three or more heavy atoms. Since the corrections for zero-point vibration are probably less accurately known than the heats of formation, the uncorrected heats of bond separation (at 0°K) are also given in parentheses. Table III gives a corresponding set of values for the energies of hydrogenation. As pointed out in the introduction, energies of complete hydrogenation for the larger molecules can be obtained by summing appropriate reaction energies in these two tables.

The results clearly indicate that all three methods calculate bond separation energies more accurately than hydrogenation energies. This is reflected in the mean absolute differences between theory and experiment shown in Table IV. It is also apparent that the extended 4-31G basis generally gives more accurate results. The minimal basis sets are unsatisfactory for the calculation of hydrogenation energies, but the results for the bond separation energies are only slightly inferior to those for the extended basis.

Table IV. Mean Absolute Deviations between Theory and Experiment (kcal mol^{-1})

	STO-3G	LEMAO-6G	4-31G
Bond separation energies[a]	5.8	4.9	3.5
Hydrogenation energies	19.4	22.2	5.5

[a] Benzene excluded.

A number of comments can be made about individual bond separation energies. The positive value for propane indicates that two adjoining C–C bonds have increased stability compared with separate bonds. This is consistent with the fact that branching increases the stability of paraffins. The (uncorrected) experimental heat of bond separation is 2.4 kcal/mol, of which 0.9 kcal/mol is attributed to differences in zero-point vibrations. However, it should be noted that the uncertainty in the vibrational frequencies of a molecule such as propane may lead to an error approaching 1 kcal/mol in the correction.

Positive bond separation energies are also found for other saturated molecules in reasonable agreement with experimental results. The values for dimethylamine and dimethyl ether are larger than for propane, a trend which is reproduced by the 4-31G calculations. A large positive bond separation is found for difluoromethane, in agreement with the well-known strengthening of C–F bonds on polyfluorinated saturated carbon atoms. The effect is largest in tetrafluoromethane. The minimal LEMAO set is apparently unsatisfactory in describing C–F interactions.

The molecules propene, propyne, acetaldehyde, and acetonitrile have methyl groups attached to unsaturated bonds. Under these circumstances, the bond separation energy is a good measure of the energy stabilization to be attributed to hyperconjugation. The calculated values are in moderate agreement with experi-

Table V. Optimum Scaling Factors for Molecules (LEMAO-4G)

Molecule	Atom	Scaling factor	Molecule	Atom	Scaling factor
Water	O	0.978	Allene	C_1	1.051
	H	1.487		C_2	1.090
Ammonia	N	0.985		H	1.335
	H	1.410	Cyclopropane	C	1.056
Methane	C	1.040		H	1.329
	H	1.317	Cyclopropene	C_1	1.063
Ethane	C	1.059		C_3	1.058
	H	1.289		(C_1)–H	1.362
Methylamine	C	1.078		(C_3)–H	1.300
	N	0.991	Benzene	C	1.069
	(C)–H	1.283		H	1.069
	(N)–H	1.389		H	1.309
Methanol	C	1.087	Difluoromethane	C	1.151
	O	0.982		F	0.987
	(C)–H	1.290		H	1.291
	(O)–H	1.486	Tetrafluoromethane	C	1.257
Fluoromethane	C	1.096		F	0.992
	F	0.985	Dimethyl ether	C	1.085
	H	1.292		O	0.984
Ethylene	C	1.056		H	1.284
	H	1.320	Acetaldehyde	C_1	1.134
Formaldehyde	C	1.122		C_{Me}	1.053
	O	0.993		O	0.988
	H	1.263		(C_1)–H	1.229
Acetylene	C	1.062		(C_{Me})–H	1.325
	H	1.400	Ketene	C_1–(H_2)	1.025
Hydrogen cyanide	C	1.093		C_2	1.164
	N	1.017		O	1.000
	H	1.378		H	1.383
Propane	C_1	1.056	Carbon dioxide	C	1.222
	C_2	1.076		O	0.996
	(C_1)–H	1.290	Dimethylamine	C	1.074
	(C_2)–H	1.262		N	0.999
Propene	C_1	1.048		(C)–H	1.280
	C_2	1.077		(N)–H	1.356
	C_3	1.059	Acetonitrile	C_1	1.115
	(C_1)–H	1.320		C_{Me}	1.058
	(C_2)–H	1.282		N	1.010
	(C_3)–H	1.293		H	1.324
Propyne	C_1	1.050	Formamide	C	1.160
	C_2	1.088		N	0.998
	C_3	1.064		O	0.980
	(C_1)–H	1.410		(C)–H	1.213
	(C_3)–H	1.301		(N)–H	1.470

ment in all cases. Stronger conjugative interaction is found for formamide as observed, although this effect is underestimated by the STO-3G basis.

For benzene, the bond separation reaction refers the energy of the molecule to that of separate double and single bonds and is therefore a good measure of the resonance energy. It is somewhat overestimated by the minimal basis sets.

Effects of cumulated double bonds are well represented by the results on allene, ketene, and carbon dioxide. The theory (particularly with the extended 4-31G basis) clearly reproduces the trend from a small negative destabilizing effect in allene to a large positive effect for carbon dioxide.

The bond separation energies of cyclopropane and cyclopropene give some indication of the strain involved in the formation of three-membered rings. All three methods give values which are rather more negative than the experimental numbers, indicating an overestimation of strain energy.

The hydrogenation energies shown in Table III are in satisfactory agreement with experimental results only for the extended 4-31G basis set. The theoretical numbers using the minimal LEMAO-6G set are all more negative than the 4-31G results. Since use of an extended basis has little effect on the energy of H_2, this indicates that the improvement between LEMAO-6G and 4-31G is primarily due to a better description of the bonds between heavy atoms.

We may also note that the 4-31G results are also more negative than experimental values (except for CH_3F). This again indicates that the theoretical energy is least satisfactory for the largest molecule. Snyder and Basch also obtained hydrogenation energies which were mostly too negative using their basis set, which is rather more extended than ours. We should emphasize, as they did, that the calculated reaction energies do not necessarily show improved agreement with experiment as the basis set is expanded, since there may be a residual difference of correlation energy between reactants and products. The single-determinant (Hartree–Fock) limits for the energies of these reactions are not yet known with sufficient accuracy to assess this matter fully.

Conclusion

The main conclusion of this work is that it is useful to divide the energy of complete hydrogenation into a bond separation energy followed by a hydrogenation energy for the products. The results show that the first part can be reasonably estimated by a minimal basis set, even though the full process is not described satisfactorily. The extended 4-31G basis, on the other hand, handles both parts well.

Since use of the extended basis involves considerable computation, it cannot easily be applied to larger organic molecules. Under these circumstances the STO-3G basis, the simpler of the two minimal basis sets, should be valuable in estimating bond separation energies. These may then be used in conjunction with more accurately known energies for the parents to predict stabilities of large organic molecules.

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Appendix

Table V reports the optimum valence shell ζ values used in this study. For computational efficiency, these were calculated using the LEMAO-4G representation. Previous work has shown such ζ's to be systematically close to the 6-Gaussian values.[9] The ζ's for all nonequivalent atoms (with the exception that hydrogen atoms attached to the same heavy atom are given the same ζ) were varied in steps of 0.01 until the total energy was minimized. Two to three optimization cycles on the complete set result in ζ's accurate to 0.003 or better. Final runs were then made with the LEMAO-6G basis using these ζ values.

(9) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, in press.

On Fluorine-19 Hyperfine Splittings in the Electron Spin Resonance Spectra of Fluorinated Aromatic Free Radicals.
II. Triphenylmethyl Radicals[1]

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Abstract: The electron spin resonance spectra of symmetrically fluorinated triphenylmethyl radicals have been obtained. The fluorine-19 hyperfine interactions have been correlated with the spin densities on the fluorine atoms calculated by an approximate MO method with the use of the two-parameter equation, $a_F = Q_{CF}{}^F\rho_C{}^\pi + Q_{FC}{}^F\rho_F{}^\pi$. The estimated values of the parameters are $Q_{CF}{}^F = -85$ and $Q_{FC}{}^F = 1043$ G. These values of the parameters are consistent to within 8% in correlating all the experimental data not only on the series of fluorinated triphenylmethyl radicals but also on another series of fluorinated aromatic radicals (see following article, part III[1b]). The estimated maximum uncertainty in the parameters is about 20%. Contrary to what has been generally assumed, the results of this investigation suggest that in aromatic radicals a_F and $\rho_C{}^\pi$ can have opposite signs. Evidence for a direct interaction between *o*-fluorine atoms and spin density on the methyl carbon atom is presented.

McConnell's relationship,[3] $a_H = Q_{CH}{}^H\rho_C{}^\pi$, has successfully related the observed proton hyperfine splittings, a_H, in the electron spin resonance (esr) spectra of aromatic hydrocarbon radicals, to the spin densities, $\rho_C{}^\pi$, in the π-electron system on the contiguous carbon atoms. $Q_{CH}{}^H$ is a proportionality constant generally determined from experiment, but which can also be calculated approximately from theory.[3] Fluorine-19, which occurs in 100% natural abundance, is a nucleus similar to the proton in magnetic moment and spin. Until recently there have been only a few esr studies on fluorinated aromatic free radicals. The results of these early esr investigations,[4-7] as well as some early nuclear magnetic resonance (nmr) studies,[8,9] indicated that the simple linear relationship

$$a_F = Q_{\mathrm{eff}}{}^F\rho_C{}^\pi \tag{1}$$

analogous to McConnells' relationship for protons may not be adequate to describe the data on fluorinated compounds.

In order to explain their nmr results on a series of fluorine-substituted aminotroponiminates, Eaton, *et al.*,[8,9] proposed a modified relationship, which we will write as

$$a_F = Q_{CF}{}^F\rho_C{}^\pi + Q_{FC}{}^F\rho_F{}^\pi \tag{2}$$

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(1) (a) Part I has been published as a communication: S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.*, **91**, 191 (1969). (b) Part III: S. V. Kulkarni and C. Trapp, *ibid.*, **92**, 4809 (1970). (c) This work was presented in part at the Symposium on Fluorine-Containing Free Radicals held during the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–12, 1969. (d) Details of this work may be found in the thesis of S. V. Kulkarni, submitted in partial fulfillment of the requirements for the Ph.D. degree, to the graduate school of Illinois Institute of Technology, Chicago, Ill., June 1969.

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(3) (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); (b) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

(4) D. H. Anderson, P. J. Frank, and H. S. Gutowsky, *ibid.*, **32**, 196 (1960).

(5) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

(6) A. Carrington, A. Hudson, and H. C. Longuet-Higgins, *Mol. Phys.*, **9**, 377 (1965).

(7) M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965).

(8) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Mol. Phys.*, **5**, 407 (1962).

(9) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Amer. Chem. Soc.*, **84**, 4100 (1962).