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(27) Recent ab initio calculations (ref 10b and K. Morokuma and H. Umeyama, *J. Am. Chem. Soc.*, **98**, 4400 (1976)) of methylamine PA values show that ΔPA values arise from CH_3-group polarization, not charge transfer, in agreement with earlier interpretations based on PA–inner shell binding energy correlations and CNDO potential models.[7,10a]

Theoretical Calculation of Steric Effects in Ester Hydrolysis

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Abstract: Steric effects in aliphatic reaction series may be represented quantitatively by E_s values derived empirically by Taft some 20 years ago. $E_s = -\log k_{rel} = -\log k/k_0$ where k is the rate constant for acid-catalyzed hydrolysis of an aliphatic ester RCOOEt and k_0 is the corresponding rate constant for CH_3COOEt. We find that $\log k_{rel} = 0.340 - 0.789\Delta SE$ where ΔSE = steric energy of $RC(OH)_3$ − steric energy of RCOOH. Steric energies were calculated by molecular mechanics using minor modifications of the Schleyer 1973 hydrocarbon force field; ΔSE values closely parallel $\Delta\Delta H_f°$ values, the differences in the corresponding enthalpies of formation. The standard deviation of E_s is 0.24 and the correlation coefficient is −0.98 for 25 esters spanning a range of 4000 in relative rates. Rates have also been calculated for a further group of 20 esters for which only qualitative information is available, and these extend the range of predicted relative rates to about 800 000. While the Taft E_s values have been generally accepted as a measure of steric effects, there has always been a concern that this empirical dissection of steric and polar effects might not be clean. The success of the present theoretical calculations lends strong support to the hypothesis that E_s values do in fact measure steric effects for alkyl groups.

The classical quantitative evaluation of steric effects is based on Taft's treatment of acid-catalyzed hydrolysis of esters.[1,2] It had been pointed out earlier by Ingold that while base-catalyzed hydrolysis is subject to strong acceleration by such electron-attracting groups as chlorine atoms, acid-catalyzed hydrolysis is relatively immune to polar effects.[3] Taft's empirical postulate is that under appropriate restrictions of structural types, $E_s = -\log k_{rel} = -\log k/k_0$ represents a quantitative estimate of steric effects. In this expression k is the rate constant for acid-catalyzed hydrolysis of any ester, RCOOEt, and k_0 the rate constant for the standard, ethyl acetate, under similar conditions. Fortunately E_s values are not very sensitive to reaction conditions. Furthermore, the same E_s values generally correlate esterification rates as well; this implies that K_{eq} is roughly constant in the series. Such is not true for all esters.[4] Taft derived further relationships of the Hammett type to treat polar effects, and the Taft steric–polar relationships have proved to be especially useful in correlating rates of reactions of aliphatic compounds.[1,5] Numerous attempts have been made to relate the Taft E_s values to sizes of groups.[1,5a] These are certainly useful for making rough approximations, and they have the important advantage of simplicity of application. However the ester systems have proved too complex for successful application of a simple analysis.

Recently we have achieved a reasonable degree of success in calculating the magnitude of the steric effects by using hydrocarbon models.[6a] We used an isoalkane $RCH(CH_3)_2$ as surrogate for ester RCOOEt and neoalkane for the tetrahedral intermediate. In fact $\log k_{rel}$ is a quite good linear function of $\Delta\Delta H_f°$. The postulate is that $\Delta\Delta H_f°$, the differences in enthalpies of formation of neoalkanes and isoalkanes in the gas phase at 298 K, will serve as a measure of the energy of steric compression on going from ester to tetrahedral intermediate.

A brief comment is in order about the relationships between steric effects and enthalpy and entropy terms. The concept of a steric correction in collision theory may be approximated by a "cone of approach" treatment, a recent example being Wipke's proposal about carbonyl additions.[7] This is at least in part an entropy factor, and accords closely with the early ideas that polar effects are to be explained by enthalpy of activation and steric effects by entropy of activation. However it has, of course, been clear for some time that steric factors can also affect enthalpy; one of the commonly used measures of strain energy is the departure of an enthalpy of formation from some norm.

The success of hydrocarbon models in treating steric effects in ester hydrolysis shows that this reaction responds primarily to an enthalpy factor. A possible explanation is that steric factors determine the relative concentrations of the tetrahedral intermediates; the overall reaction rates, of course, depend directly on these concentrations. Other reactions may show a greater dependence on cone of approach. For example, SN2 closure to five-membered rings is usually faster than to six-membered rings, but the enthalpic strain energies lie strongly in favor of the six-membered rings.

In the ester hydrolysis there is clearly a favorable cancellation of entropy effects, and also of solvation effects which may comprise both enthalpy and entropy. Evidently conditions at the ester group and at the tetrahedral intermediate are relatively constant from one ester to another, or else the effects are proportional to the steric effects.

Alkane models have one major advantage: the alkane force fields have been relatively well established.[8] They have the

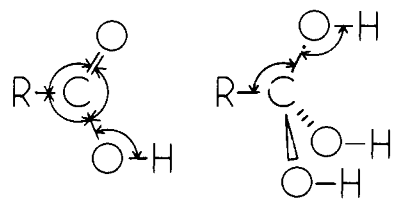


Figure 1. Geometry used for carboxylic acid and for ortho acid models. RCOOH bond lengths: C=O, 1.23; C—O, 1.36; O—H, 1.00. Bond angles: R—C=O, 120°; R—C—O, 115°; C—O—H, 115°. $RC(OH)_3$ bond lengths: C—O, 1.42. Bond angles: R—C—O, 110°; C—O—H, 110°. Actually the hydroxyl hydrogens might as well have been omitted since they were placed so as to be remote from the R group.

obvious disadvantage of representing the steric properties of the reaction center rather roughly. The purpose of the present study is to seek a better approximation. We chose the carboxylic acid as the model for steric effects in the ester and the ortho acid for steric effects in the tetrahedral intermediate. As discussed earlier, many rather approximate models of the transition state may be expected to work reasonably well,[9,13] and fortunately the success of the calculation does not depend on knowing whether we are modeling transition state or tetrahedral intermediate.

$$RCOOEt \rightarrow RC(OH)_2OEt \rightarrow \text{products}$$

$$RCOOH \rightarrow RC(OH)_3$$

We chose to work with the Schleyer 1973 force field[8] since this is appreciably simpler than the Allinger 1971 force field[10] and requires somewhat less computer time. Since no force field values were available for oxygen atoms, we made several approximations as summarized in Figure 1. These involve adoption of rigid geometries, planar for RCOOH and tetrahedral for $RC(OH)_3$. Furthermore the R-C bond length and force constant were set equal to the values for a C-C alkane bond and the carbon atom nonbonded potential functions were used for oxygen atoms. In one sense these choices are oversimplified. We could instead make reasonable guesses about appropriate constants for oxygen atoms and for carbonyl carbon atoms. However it has been our approach to seek the simplest possible models which work, and there are several factors to support the choices we made.

Since hydrocarbon models work relatively well, by extension any group that roughly approximates the ester tetrahedral intermediate sites will also work. The acid-ortho acid models are considerably closer to the reactants and the intermediates in steric properties than are the hydrocarbons, and therefore they should be better. Evidently details of deformability of bonds at the ester and at the tetrahedral intermediate play only a minor role, else the hydrocarbon models could not succeed. Thus in the absence of well-tested oxygen values we chose to add no new constants to the force field for the present study.

The energy computed by the moleculer mechanics force field is called the steric energy of the conformation of the molecule.[8,10] It is possible to relate the steric energy to the enthalpy of formation by adding to the steric energy a base $\Delta H_f°$ value which depends on an inventory of the structural elements present such as CH_3, CH_2, COOH, etc., plus a statistical mechanical term to represent energy contributions of other conformations of generally similar energies.[6a] Although steric energy may be similar to strain energy, steric energy values also contain base value contributions that depend on just how the force field has been defined. It is possible to effect a dissection of the steric energy into the base value and the strain energy if this is desired.[6b]

The difference in enthalpy of formation of ortho acid $RC(OH)_3$ and of carboxylic acid RCOOH is therefore representable by

$$\Delta\Delta H_f° = \Delta SE + \Delta SM + \Delta base\Delta H_f° \text{ values} \qquad (1)$$

For each pair having a common R group, the $\Delta base\Delta H_f°$ values term will be identical by definition. The statistical mechanical difference will generally be constant to within about 0.2 kcal/mol.[6b] Hence the enthalpy difference is quite well represented by the ΔSE term alone.

Results and Discussion

In Table I are presented the steric energy values obtained with the modified Schleyer 1973 force field along with literature values of log k_{rel} and the values of log k_{rel} calculated from

$$\log k_{rel} = 0.340 - 0.789SE \qquad (2)$$

The standard deviation of the fit is 0.24 and the correlation coefficient is −0.98. The fit is good in terms of linear free energy relationships, and useful since the predicted rates have a relative standard deviation of about 1.7. See also Figure 2. It is interesting that the slope is roughly 1/1.36 (= 0.73) the value that would correspond to $\Delta G = \Delta H = \Delta SE$ at 298 K.

We may usefully evaluate the significance of the error terms in the last column with reference to (1) limitations of the model, (2) limitations of the force field, (3) errors in the calculations, and (4) errors in the experimental data.

All kinetics data represent some sort of abstraction: rates are not exactly proportional to concentration of catalyzing acid, relative rates differ in different solvents and at different reaction temperatures, and so on. The model is certainly limited in that it takes no explicit account of solvation nor of entropic effects. The log k_{rel} values are uncertain in that they represent averages over some limited set of experimental conditions and might well have different values if based on other sets. Internal consistency of the original kinetics data indicates a standard deviation of perhaps 0.05 to 0.1 for most log k_{rel} values in Table I.

Errors in calculations may be of three types: (a) failure to enter data completely and correctly, (b) inadequate convergence, and (c) failure to find the conformation of minimum energy. The procedures we have established for generating the input data are computer assisted and reliable, and convergence errors at worst are estimated to be no larger than 0.05 in ΔSE. Searching for local minima requires care. For all compounds we based the search on examination of physical models, and we showed that different starting conformations led to a consistent set of local minima. In cases of fairly large delta values we carried out a careful reexamination for possible computational errors. We believe that the calculated values are correct to 0.05 kcal/mol.

We also looked for consistency of results. For example, the calculated log k_{rel} for ethyl isovalerate (R = *i*-Pr) is −1.01 which is 0.54 too small. A way to check this result is to examine related compounds. One such is ethyl β-methyl-*n*-valerate (R = *sec*-Bu) for which the calculated log k_{rel} is −1.22, which is acceptable (0.09 low). Examination of models shows that the extra methyl is remote from the ester and that the two compounds should indeed have nearly the same log k_{rel} (as was found). In this particular example we conclude that the experimental data may well be in error.

In examining errors arising from the force field we must be clear about definitions. The energy term resulting from the molecular mechanics minimization is called a steric energy. The energy required by the model, however, is a strain energy which reflects steric crowding. The relationship between steric energy and strain energy was discussed above, and in more detail elsewhere.[6b] Any force field represents an approximation limited by numerous compromises. We have shown that the

Table I. Calculation of Relative Rates of Acid-Catalyzed Hydrolysis of Esters $RCOOC_2H_5$

Ester R–	log k_{rel}[a] obsd	SEA[b] RCOOH, kcal/mol	SEO[b] $RC(OH)_3$, kcal/mol	ΔSE SEO – SEA	log k_{rel}[c] calcd	Δ[d]
Me–	0.000	0.25	0.25	0.00	0.34	–0.34
Et–	–0.07	1.17	2.14	0.97	–0.42	0.35
Cyclobutyl–	–0.06	25.38	25.95	0.57	–0.11	0.05
n-Pr–	–0.36	1.66	2.59	0.93	–0.39	0.03
n-Bu–	–0.39	2.22	3.13	0.91	–0.38	–0.01
n-Pentyl–	–0.40	2.79	3.69	0.90	–0.37	–0.03
Isopentyl–	–0.35	3.56	4.47	0.91	–0.38	0.03
n-Octyl–	–0.33	4.51	5.40	0.89	–0.36	0.03
Neopentyl–CH_2–	–0.34	4.68	5.59	0.91	–0.38	0.04
i-Pr–	–0.47	2.33	4.04	1.71	–1.01	0.54
Cyclopentyl–	–0.51	11.51	12.49	0.98	–0.43	–0.08
Cyclohexyl–	–0.79	6.05	7.57	1.52	–0.86	0.07
i-Bu	–0.93	2.45	4.08	1.63	–0.95	0.02
Cyclohexyl–CH_2–	–0.98	6.19	7.75	1.56	–0.89	–0.09
s-Bu–	–1.13	3.75	5.73	1.98	–1.22	0.09
Cycloheptyl–	–1.10	13.43	15.43	2.00	–1.24	0.14
t-Bu–	–1.54	4.36	5.97	1.61	–0.93	–0.61
Neopentyl–	–1.74	3.35	6.06	2.71	–1.80	0.06
Neopentyl–$CH(CH_3)$–	–1.85	8.47	10.73	2.26	–1.44	–0.41
Et_2CH–	–1.98	4.80	8.09	3.29	–2.25	0.27
n-Pr_2CH–	–2.11	5.75	8.92	3.17	–2.16	0.05
i-Bu_2CH–	–2.47	7.89	11.49	3.60	–2.50	0.03
Neopentyl–$C(CH_3)_2$–	–2.57	13.37	15.59	2.22	*e*	
(Neopentyl)$_2$–CH–	–3.18	11.14	17.66	6.52	*e*	
t-$BuCH(CH_3)$–	–3.33	7.29	12.21	4.92	–3.54	0.21
t-$BuC(CH_3)_2$–	–3.90	13.60	18.58	4.98	–3.59	–0.31
Et_3C–	–3.80	11.45	16.54	5.09	–3.67	–0.13
Neopentyl–C(*t*-Bu)(CH_3)–	–4.00	22.57	30.37	7.80	*e*	

[a] $k_{rel} = k/k_0$ where k is rate constant for any ester and k_0 is rate constant for ethyl acetate. [b] Steric energy of carboxylic acid (or ortho acid) defined by modified Schleyer 1973 alkane force field. [c] From eq 2. [d] log k_{rel}(obsd) – log k_{rel}(calcd). [e] Value not reliably determined by the force field. See text.

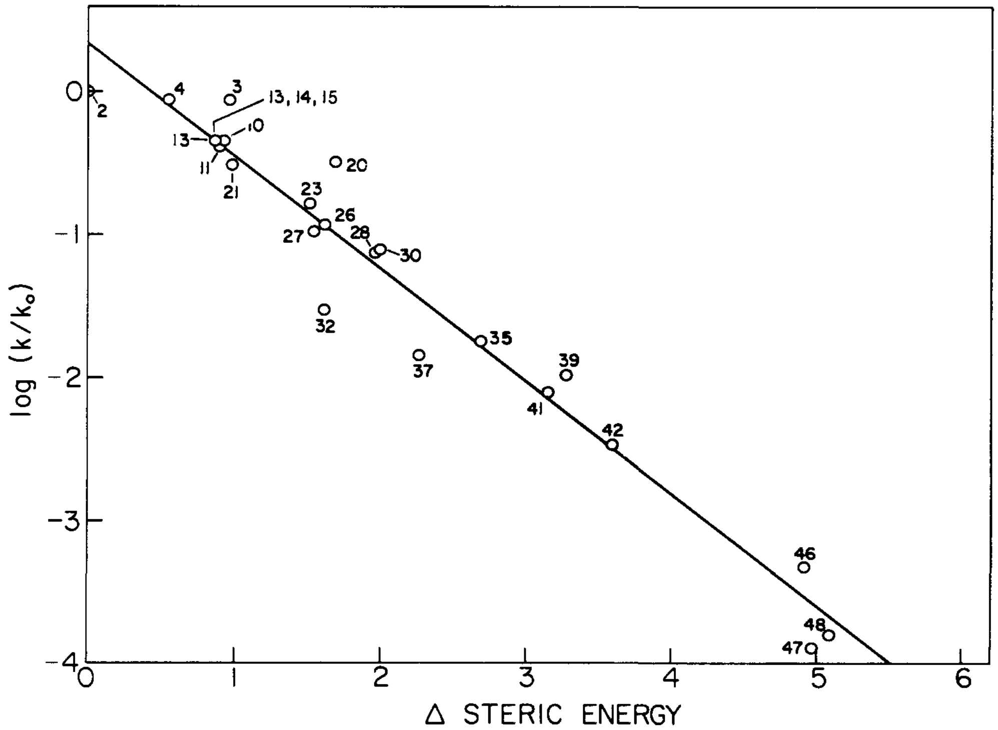
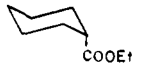
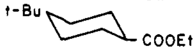
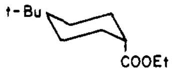
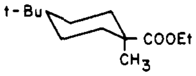
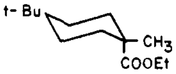
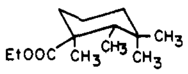
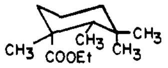
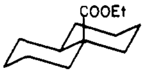
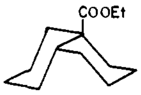
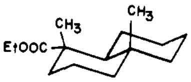
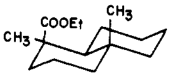
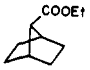
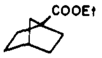
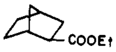
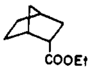
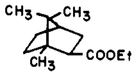
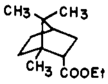
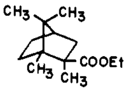
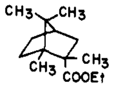


Figure 2. Linear free energy correlation of E_s (= log k_{rel}) for acid-catalyzed hydrolysis of esters vs. ΔSE (= steric energy for ortho acid – steric energy for acid). The numbers correspond to the Taft table (ref 1).

Schleyer force field reproduces strain energies with a standard deviation of about 1.0 kcal/mol.[6b] Our ad hoc modifications would presumably increase this error somewhat.

The important question, though, is what error to assign to the ΔSE values. We note first that ΔSE is a true strain energy difference plus a small base value term which is the same for every ester. Suppose that we ask what error in ΔSE corresponds to a standard deviation of 0.24 in log k_{rel}: the answer is roughly 0.3 kcal/mol. However since other factors contribute to the error in log k_{rel}, perhaps only 0.25 kcal/mol is ascribable to errors in ΔSE. The expected error on zeroth order grounds would be about 1.4 (for a difference in two SE values). How-

Table II. Predicted Relative Rates of Acid-Catalyzed Hydrolysis of Esters

		For RCOOH		For RC(OH)$_3$				
	Ester	Torsion	SEA	Torsion	SEO	ΔSE	log k_{rel}	10^5 k_{rel}
1.		299	6.04	178	7.57	1.53	−0.87	13 500
2.		294	8.02	174	10.02	2.00	−1.24	5 750
3.		300	12.63	178	14.09	1.46	−0.81	15 500
4.		290	14.45	173	16.38	1.93	−1.18	6 600
5.		15	16.44	181	18.39	1.95	−1.20	6 300
6.		26	15.44	176	19.38	3.94	−2.77	170
7.		121	19.75	194	23.96	4.21	−2.98	105
8.		359	18.91	178	25.57	6.66	−4.91	1.23
9.		1	14.60	180	21.97	7.37	−5.47	0.34
10.		18	15.38	182	20.51	5.13	−3.71	19.5
11.		124	22.67	195	26.54	3.87	−2.71	190
12.		5	21.28	185	28.46	7.18	−5.33	0.47
13.		32	22.84	191	25.82	2.98	−2.01	980
14.		0	21.51	180	22.68	1.17	−0.58	26 300
15.		331	21.88	181	22.98	1.10	−0.53	29 500
16.		345	22.25	196	23.69	1.44	−0.80	15 800
17.		254	31.22	192	34.08	2.86	−1.92	1 200
18.		336	29.61	192	32.09	2.48	−1.62	2 400
19.		44	36.59	198	44.25	7.91	−5.90	0.126
20.		13	36.66	190	42.81	6.15	−4.51	3.1

ever on going from RCOOH to RC(OH)$_3$ we have only a differential increase in strain, and because we are actually working with double differences, there will be further cancellation of systematic errors contributed by the force field. We would have guessed a priori that the differential error might be perhaps 30% of the primary error, and the observed 20% figure is certainly acceptable.

In summary, the calculations of the steric factors work out much better than we have any right to expect. The question in the long run will be how well values calculated by eq 2 will correspond to data based on more comprehensive series of compounds and of reaction conditions. We turn next to consider the range of proper applicability of eq 2.

There are important restrictions as to reaction type, as was clearly recognized by Taft.[1] The cancellation of base $\Delta H_f°$ values shown in eq 1 requires that resonance effects be absent (or constant). This means that separate series must be used for conjugated unsaturated esters, for aryl carboxylic acid esters, and for substituted acetic acid esters. Likewise ethyl formate will not be expected to correlate because the HC bond hybridization introduces a new factor different from $R_3CCOOEt$.

$-\underset{|}{C}=\underset{|}{C}-COOEt \quad ArCOOEt \quad R_3CCOOEt$

There is also a limit on the Schleyer 1973 force field which makes it inapplicable to several of the more interesting highly strained esters. The problem arises in part from the cubic correction term in the definition of the angle deformation energy. As an angle opens, the effective force constant decreases. In highly strained (neopentyl)$_2$-CHCOOH, for example, the C-C-C angle opens to the implausible value of 170°.

Schleyer has pioneered the use of molecular mechanics in treating strain energies of solvolysis reactions and has correlated rates spanning some 25 powers of ten.[12] The solvolysis series is especially favorable since strain in the reactant is largely relieved in the intermediate "carbon cation". Steric effects enter ester hydrolysis in a less favorable differential sense: in order to realize a large steric effect, both ester and intermediate must be strained. In the range of structures where interesting rate differences are observed, both experiment and calculation begin to encounter difficulties. Ester formation also is subject to steric acceleration,[4] and preliminary calculations using hydrocarbon models show the promise of molecular mechanics in this area.[13] Molecular mechanics has also been applied to aldol condensation reactions.[14]

We have extended the calculations to predict relative rates of hydrolysis of esters of interest in conformational analysis, and results are summarized in Table II. The slowest of these, compound **19**, has a predicted rate a factor of some 800 000 slower than ethyl acetate. Relative rate data are available for the methyl 4-*tert*-butylcyclohexanecarboxylates **3** and **4**.[15] The reported k_{eq}/k_{ax} is 4.8 in 50% aqueous dioxane at 90 °C. Our predicted value is 2.4 for 70% aqueous acetone at 25 °C. The relative rates are not greatly affected by reaction conditions.[2,5] This agreement is good in terms of usual linear free energy correlations.

The axial-equatorial conformational energy differences are in the expected ranges for the relative sizes of the -COOH and -C(OH)$_3$ groups. The carboxyl group is roughly similar in size and symmetry to isopropyl and the -C(OH)$_3$ group is a little larger than methyl and has the same local C_3 symmetry. The equatorial -COOH has a lower energy than the axial by 1.8-2.0 kcal/mol, a value comparable to the 2 kcal/mol free energy difference for the isopropyl group.[16,17] The -C(OH)$_3$ group shows a slightly larger value, about 2.3. In the series **1-4**, the relative constancies of the computed energy differences lend support to the use of the 4-*tert*-butyl group to "freeze" a molecule in a preferred conformation as suggested by Winstein.[18]

There are, however, specific interactions whose effects are less easily predicted; these occur where multiple substitution is present or where ring structures force certain conformations. Examples are found among compounds **7-12**. The planar carboxyl group can often achieve an orientation which partly escapes crowding whereas a group with local C_3 symmetry cannot. Thus an axial COOH has a slightly lower energy than an axial CH$_3$ in the pair **7** and **8**. The C(OH)$_3$ group, being larger than -CH$_3$, shows the expected order in the pair **7** and **8**.

Analyses along these lines can be presented for each of the pairs. We comment briefly on just one further example, the decalin-9-carboxylic acid pair **9** and **10**. *trans*-Decalin is more stable than cis by 3.1 kcal/mol (difference in $\Delta H_f°$);[19] Schleyer reports a steric energy difference of 2.7 from his force field.[8] A 9-methyl substituent lowers the difference to about 0.6-1.4 kcal/mol,[20,21] and the difference in the two acids **9** and **10** is 0.78, in good agreement. The reversal for the RC(OH)$_3$ pair represents a continuation of the trend. The formulas as written show the positions of four axial hydrogen atoms in **9** and two (or three) in **10** near the substituent, and the local threefold symmetry of the -C(OH)$_3$ group makes it impossible to find a rotation that removes these interferences.

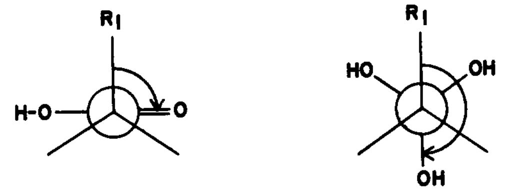
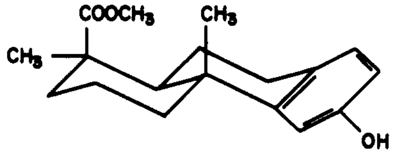


Figure 3. Definition of conformational torsion at energy minimum. (See Table II.) The torsion shown is for the R group for RCH_2COOH and for the largest R in $R_1R_2R_3CCOOH$. For $R_1R_2CHCOOH$ the carbonyl group is flanked by R$_1$ and R$_2$.

The methyl ester of podocarpic acid **21** is reported to be especially resistant to hydrolysis.[22] This molecule is analogous to ester **12**. The epimeric equatorial ester hydrolyzes with relative ease. The predicted ratio of rates is 400, but the faster ester is predicted to hydrolyze about 500 times more slowly than ethyl acetate.



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There has been some interest in preferred conformations of planar groups connected to sp^3 carbon.[23] The angles assumed by the carboxyl group are given in Table II and are defined in Figure 3. For purposes of the present calculations the intrinsic barrier to rotation was set at zero, and the effective barrier is the weak one imposed by the nonbonded interactions. Except for highly crowded molecules these are relatively small. In fact, the crystal structure of sodium hydrogen diacetate shows an unusually large amplitude of libration of the carboxyl groups, further indication of a low barrier.[24]

Calculations

The molecular mechanics calculations were carried out by the program MOLMEC whose reliability has been carefully checked.[6] The starting conformations were selected by examination of Dreiding models, and in cases of doubt energies were calculated for several initial conformations. MOLMEC carries out adjustments on all or on any desired selected set of internal coordinates. The steric energy was minimized to a final step size of 0.01% or less. Resulting steric energies are generally reliable to better than 0.1%.

The Schleyer 1973 force field was used.[8] The fixed geometries selected for the carboxyl group and the ortho acid group are shown in Figure 1. The carbon nonbonded potential functions were used for oxygen atoms. The intrinsic barrier to rotation about the R-C bond of RCOOH and of RC(OH)$_3$ was set at zero.

Parameter adjustments for eq 2 were carried out with the program GENLSS.[25]

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Generalized Valence Bond Description of the Low-Lying States of NiCO[1]

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Abstract: GVB and GVB-CI wave functions (using a double ζ basis) have been obtained as a function of internuclear distance for the lowest three states of NiCO. The wave functions lead to a qualitative description in which the Ni atom is neutral with a $(4s)^1(3d)^9$ atomic configuration. The CO lone pair delocalizes slightly onto the Ni leading to the 4s-like orbital hybridizing away from the CO. The dπ pairs on the Ni are slightly back-bounding to the CO. The three bound states are $^3\Sigma^+$, $^3\Pi$, and $^3\Delta$ consisting of the singly occupied 4s-like orbital plus a single d hole in a σ, π, or δ orbital, respectively. The ground state is found to be $^3\Delta$ with calculated $R_e = 1.90$ Å, $D_e = 1.15$ eV = 26.5 kcal/mol, and ω_e(Ni-C) = 428 cm^{-1}, all reasonable values, although direct information on NiCO is not yet available. The adiabatic excitation energies are calculated as 0.240 eV to $^3\Sigma^+$ and 0.293 eV to $^3\Pi$. The states with $(4s)^2(3d)^8$ configurations on the Ni lead to repulsive potential curves with vertical excitation energies in the range of 3.0 to 5.0 eV.

I. Introduction

The study of the reactions occurring at metal surfaces constitutes an important field of modern chemical research. As one step in a program directed toward understanding one such reaction, the methanation of CO on a nickel surface, we are investigating the bonding of CO to the surface. As the first step of examining the bonding of CO to a Ni surface, we have carried out extensive studies of the bonding of CO to a single Ni atom. These results will be useful in understanding how to study the bonding of CO to larger complexes and indeed already provide some useful insights into the nature of the bond to the surface.

In addition, matrix isolation experiments have provided evidence for the existence of Ni(CO)$_n$, $n = 1$-4.[3] It is expected that the results of the NiCO calculations will suggest some experimental tests for these model systems.

In section II we describe basic concepts of the GVB wave functions, the effective potential, and the basis set used. In section III the results obtained are discussed in qualitative terms, while section IV examines in more detail some of these concepts in terms of the GVB wave function. Section V discusses the excited states. In section VI we describe the CI calculations. Section VII compares results with the ab initio effective potential (AIEP) and the modified effective potential (MEP) used here.

II. The Wave Functions

A. The GVB Method. The details of the GVB method have been described elsewhere.[4] The GVB wave function can be viewed as a normal closed-shell Hartree-Fock (HF) wave function,

$$\mathcal{A}(\phi_1\phi_1\alpha\beta\phi_2\phi_2\alpha\beta\ldots)$$

in which certain doubly occupied singlet pairs

$$\phi_i\phi_i\alpha\beta \tag{1}$$

are replaced by GVB pairs

$$(\phi_{ia}\phi_{ib} + \phi_{ib}\phi_{ia})\alpha\beta = (\lambda_1\phi_{i1}{}^2 - \lambda_2\phi_{i2}{}^2)\alpha\beta \tag{2}$$

where each electron of the pair is allowed to have its own GVB orbital ϕ_{ia} or ϕ_{ib}, the overlap of which,

$$S_{ab}{}^i = \langle\phi_{ia}|\phi_{ib}\rangle \tag{3}$$

is in general nonzero. In the perfect pairing approximation to GVB (referred to as GVB-PP), the GVB orbitals of a given pair are taken as orthogonal to those of all other pairs (strong orthogonality restriction) and in addition the spin eignfunction is restricted to the form where the maximum number of pairs are singlet coupled (perfect pairing restriction). For nonsinglet states we also allow n high coupled orbitals.