$(r_{V_{\max}})$. The steric effect of the latter group on pK^d_{HA} of benzoic acids in aprotic solvents was shown to be negligible.[3]

The small value of pK^d_{HSal} of 16.7 as compared to pK^d_{HBz} of 20.7 in AN is partly due to relatively weak intramolecular hydrogen bonding in the acid and a much stronger intramolecular hydrogen bond in the anion on the one hand and the electron-releasing inductive effect of the *o*-hydroxyl group on the other. A similar situation exists in DMSO and DMF.

Acknowledgment. We are indebted to Professor M. M. Kreevoy for helpful discussion of the infrared spectra.

A Comparison of the CNDO and Mulliken Semiempirical Molecular Orbital Methods[1]

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Abstract: The CNDO/2 method is related to the Mulliken method. Application of similar parameter schemes in both approaches is discussed and applied to calculations of several simple organic molecules including acetylene, ethylene, ethane, and cyclobutane.

The primary goal for most *ab initio* quantum mechanical molecular calculations is the exact determination of whatever molecular property one is interested in by the use of as refined a mathematical approach as is necessary for the physical problem. Semiempirical calculations generally have a more limited and often more contradictory set of goals. The major consideration for them has been the gross simplification of *ab initio* methods in such a way as to reduce the time and effort necessary to obtain wanted results for large systems. A second consideration, perhaps more important in the future, has been the conceptual utility of methods which give insight into the important qualitative and semiquantitative propositions of chemistry rather than just a numerical solution as exact *ab initio* results are wont to be.

Semiempirical methods generally have attempted to solve the Hartree–Fock SCF equations by using various assumptions to reduce the volume of integral computations. In addition, parameters for these calculations have usually been based on experimentally observed quantities with the aim in mind of compensating for the electron correlation deficiencies of the Hartree–Fock method. Moreover, the methods were usually intended for a fairly limited set of applications such as dipole moments, geometries, reactivities, spectra, or thermodynamic stabilities and could not really be expected to be valid for all applications or even all cases within an application.[2a]

In this context it is important to evaluate parameter sets and methods with respect to each other so that their applicability and limitations become clearer, and so that the "chemical" consequences of the parametrization become more evident. A great deal of interest has been shown in semiempirical calculations performed by the CNDO/2 method, which was parametrized to make results agree with Hartree–Fock calculations.[2] Somewhat less interest has been shown in calculations performed by Mulliken-type methods both of the SCF and non-SCF type.[3] The severe approximations of the CNDO method and possible approximations for other semiempirical methods have been discussed by a number of workers.[4–6] However, results by Mulliken and CNDO methods have not in general been compared, although the use of Mulliken approximations to lesser or greater extents within various methods is extensive (*e.g.*, ref 2a and 3–6).

Both methods are correct only to the first order in overlap by the *S*-expansion technique.[5] The similarity of the two methods may be seen by the following treatment, where the CNDO method is shown to be related to the Mulliken method.

In the Mulliken method, the Hartree–Fock matrix[7]

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \tag{1}$$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu/\lambda\sigma) - \tfrac{1}{2}(\mu\sigma/\lambda\nu)] \tag{2}$$

where

$$\mathbf{FC} = E\mathbf{SC} \tag{3}$$

is approximated by

$$H_{\mu\nu} = \tfrac{1}{2}(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} \tag{4}$$

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(2) (a) See, for example "Sigma Molecular Orbital Theory," K. B. Wiberg and O. Sinanoğlu, Ed., Yale University Press, New Haven, Conn., 1970, for a compendium of calculations performed by various MO methods; (b) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

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(7) The notation is similar as far as possible to that of ref 2b.

$$(\mu\nu/\lambda\sigma) = {}^1/_4 S_{\mu\nu}S_{\lambda\sigma}[(\mu\mu/\lambda\lambda) + (\mu\mu/\sigma\sigma) + (\nu\nu/\lambda\lambda) + (\nu\nu/\sigma\sigma)] \quad (5)$$

If it is assumed as in CNDO that $(\chi\chi/\phi\phi)$ is calculated between s orbitals on the corresponding centers, these integrals can be written[6]

$$(\mu\nu/\lambda\sigma) = {}^1/_4 S_{\mu\nu}S_{\lambda\sigma}[\gamma_{AC} + \gamma_{AD} + \gamma_{BC} + \gamma_{BD}] \quad (6)$$

If $H_{\mu\mu}$ is set equal to the CNDO value

$$H_{\mu\mu} = \epsilon_\mu + {}^1/_2\gamma_{AA} - \sum_C Z_C\gamma_{AC} \quad (7)$$

where

$$\epsilon_\mu = -{}^1/_2(I + A) \quad (8)$$

then $H_{\mu\nu}$ is

$$H_{\mu\nu} = {}^1/_2 S_{\mu\nu}\{\epsilon_\mu + \epsilon_\nu - \sum_C Z_C(\gamma_{AC} + \gamma_{BC}) + {}^1/_2(\gamma_{AA} + \gamma_{BB})\} \quad (9)$$

The positive terms of the electron repulsion matrix

$$R_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\nu/\lambda\sigma) = \sum_{\lambda\sigma} {}^1/_2 P_{\lambda\sigma}S_{\lambda\sigma}\{(\mu\nu/\lambda\lambda) + (\mu\nu/\sigma\sigma)\} \quad (10)$$

sum to give

$$R_{\mu\nu} = \sum_\lambda q_\lambda(\mu\nu/\lambda\lambda) \quad (11)$$

where q is the charge of orbital λ defined in the normal Mulliken manner. A similar result applies for the negative term $q_\mu(\mu\mu/\mu\mu)$, but in general the negative terms do not contribute in such a direct manner. The resultant matrix elements may be written (where $G_{\mu\nu}{}^R$ represents the sum of residual contributions of the negative terms)

$$F_{\mu\nu} = {}^1/_2(\epsilon_\mu + \epsilon_\nu)S_{\mu\nu} + {}^1/_2\sum_C(Q_C - Z_C)(\gamma_{AC} + \gamma_{BC})S_{\mu\nu} - {}^1/_2\{{}^1/_2(q_\mu - 1)\gamma_{AA} + {}^1/_2(q_\nu - 1)\gamma_{BB}\}S_{\mu\nu} - G_{\mu\nu}{}^R \quad (12)$$

or in abbreviated form

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu}{}^M - G_{\mu\nu}{}^R \quad (13)$$

For the diagonal terms, eq 12 reduces formally to the familiar CNDO/2 expression if $G_{\mu\mu}{}^R$ is neglected.

It must be emphasized that merely the numerical value of the term is being discussed. The normalization of the CNDO and Mulliken wave functions is of course different. The consequences of using these particular numerical values can then be examined.

The energy as calculated by CNDO/2 may be partially evaluated in terms of Mulliken bond orders if charges by both methods are set equal as noted. This energy is a sum of diagonal and off-diagonal terms. Letting $P_{\mu\nu}{}^C$ represent the CNDO bond orders, the diagonal terms may be expressed

$$E_D = {}^1/_2\sum_\mu P_{\mu\mu}{}^C(2H_{\mu\mu} + G_{\mu\mu}{}^M) \quad (14)$$

Here $G_{\mu\mu}{}^M$ represents only the dominant terms as defined above. Expressing this in terms of Mulliken bond orders and remembering the definitions of $H_{\mu\nu}$ and $G_{\mu\nu}$ in the Mulliken framework

$$E_D \simeq {}^1/_2\sum_\mu\sum_\nu P_{\mu\nu}S_{\mu\nu}(2H_{\mu\mu} + G_{\mu\mu}{}^M) = {}^1/_2\sum_\mu\sum_\nu P_{\mu\nu}(2H_{\mu\nu} + G_{\mu\nu}{}^M) \quad (15)$$

Thus the diagonal terms include most of the energy. The off-diagonal energy contributions in CNDO/2 are given by

$$E_{OD} = {}^1/_2\sum_\mu\sum_\nu P_{\mu\nu}{}^C(2\beta_{\mu\nu}S_{\mu\nu} - {}^1/_2P_{\mu\nu}{}^C\gamma_{AB}) \quad (16)$$

The difference between the Mulliken energy and the CNDO/2 energy may be examined. While the two energies should not be expected to be identical, variations in behavior of the energies which do not seem to be physically based should be suspect. Thus

$$\Delta E = E_{CNDO} - E_{Mull} \simeq \sum_{\mu\nu} P_{\mu\nu}G_{\mu\nu}{}^R + {}^1/_2\sum_{\mu\nu} P_{\mu\nu}{}^C(2\beta_{\mu\nu}S_{\mu\nu} - {}^1/_2P_{\mu\nu}{}^C\gamma_{AB}) \quad (17)$$

The variation of this ΔE term with molecule type would appear to be of interest in the understanding of results by the CNDO/2 method.

Calculations

In order to obtain a set of calculations where the parallelism of CNDO/2 and the Mulliken approach can be compared as closely as possible, it was felt that as few parameter changes as possible should be made on going from one approach to the other. Several problems are immediately apparent in this venture.

One arises from the unsatisfactory assumption of the Mulliken method as given above that the off-diagonal kinetic energy terms are approximated by

$$T_{\mu\nu} = {}^1/_2 S_{\mu\nu}(T_{\mu\mu} + T_{\nu\nu}) \quad (18)$$

This problem is compounded by the fact that in the CNDO/2 method the bond integrals are taken as completely empirical parameters and thus comparison between the methods is made somewhat more difficult.

As a solution which is not wholly satisfactory, an empirical function was sought which would approximate the difference between the true value of $T_{\mu\nu}$ and the approximate one. The difference function should approach zero as the internuclear distance approaches zero or infinity. In addition, because the methods are based on s-orbital potentials, so should the difference function be.

The function decided upon, $D_{\mu\nu}$, has approximately the correct functional behavior for s orbitals in the region of interest (Table I). For p orbitals it is not as good, but $H_{\mu\nu}$ seems to be adequately approximated by its use (Table II). In any case since we were looking for the *pattern* of differences it was not felt that, in view of the many other approximations made in the CNDO/2 method, there was much to be gained by further search. Clearly, better parameter schemes for both CNDO and Mulliken methods are possible.[2a]

$$D_{\mu\nu} = 0.85[2\gamma_{AA}\gamma_{BB} - (\gamma_{AA} + \gamma_{BB})\gamma_{AB}]S_{\mu\nu} \quad (19)$$

Since the Mulliken method is a full-overlap method and it would appear (*vide infra*) that the use of $V_{AB} = Z_B\gamma_{AB}$ in the CNDO/2 method is in part a compensation for the approximations in it, we felt that $V_{AB} = Z_B \cdot (S|1/r_B|S)$ might be a more appropriate term in the Mulliken method, as first proposed for CNDO/1.[8]

Table I. Variation of $T_{\mu\nu}$ and $D_{\mu\nu}$ with Bond Type and Distance (au)

Bond	Distance, Å	True T	Mulliken T	Corrected T	D	$D/0.85$
H–H	0	0.720	0.720	0.720	0	0
	1.32	0.036	0.264	0.070	0.194	0.224
	1.76	−0.006	0.138	0.017	0.121	0.143
	2.64	−0.012	0.033	−0.002	0.035	0.041
C_{2s}–C_{2s}	0	0.440	0.440	0.440	0	0
	1.30	0.076	0.201	0.103	0.098	0.115
	1.95	−0.008	0.082	0.022	0.060	0.071
	2.60	−0.011	0.029	0.003	0.026	0.030
C_{2s}–H	1.03	0.132	0.320	0.187	0.133	0.156
C_{p_z}–H	1.03	0.301	0.515	0.394	0.121	0.142
C_{p_z}–C_{p_z}	1.54	0.255	0.434	0.348	0.086	0.101
C_{p_z}–C_{2s}	1.54	0.115	0.321	0.226	0.095	0.112
C_{p_x}–C_{p_x}	1.54	0.054	0.253	0.203	0.050	0.059
C_{2s}–C_{2s}	1.54	0.030	0.150	0.062	0.088	0.104

Table II. Sample Values of $H_{\mu\nu}$ in the Mulliken Approximation[a]

Orbitals A	Orbitals B	Distance	Mulliken	CNDO/2[b]	Theoretical
2s	2s	1.54	−39.01	−38.57	−42.05
$2p_z$	$2p_z$	1.54	−34.89	−37.26	−39.21
$2p_z$	2s	1.54	−40.27	−41.36	−44.99
$2p_x$	$2p_x$	1.54	−20.37	−21.75	−19.14
2s	H	1.03	−46.50	−43.57	−48.95
$2p_z$	H	1.03	−40.38	−39.84	−39.35
2s, 2s			−70.26	−70.26	−76.44
2p, 2p			−61.78	−61.78	−52.50

[a] Integrals at 1.54 Å represent C–C bonds, integrals at 1.03 Å represent C–H bonds. Theoretical: $H_{\mu\nu} + T_{\mu\nu} + V_{\mu\nu}{}^{A} + V_{\mu\nu}{}^{B}$. Mulliken: $H_{\mu\nu} = (\epsilon_\mu + \epsilon_\nu)S_{\mu\nu}/2 - [(Z_A - {}^1/_2)\gamma_{AA} + (Z_B - {}^1/_2)\cdot\gamma_{BB}]S_{\mu\nu}/2 - D_{\mu\nu} + (Z_A V_{AB} + Z_B V_{BA})S_{\mu\nu}/2$. [b] Value of term assuming cancellation as given by eq 12, 21, and 22 has not taken place implicitly. Note that this value of $H_{\mu\nu}$ should not be used for energy determination, since in effect it has been taken care of in the diagonal energy terms. $H_{\mu\nu}' = \beta_{\mu\nu}{}^0 S_{\mu\nu} - [(Z_A - {}^1/_2)\gamma_{AA} + (Z_B - {}^1/_2)\gamma_{BB}]S_{\mu\nu}/2 - (Z_A + Z_B)\gamma_{AB}S_{\mu\nu}/2$.

The calculations were performed with modified versions of QCPE Program No. 185.[9] In addition to some preliminary calculations, a range of calculations was performed. Calculations using CNDO/2 comprised one extreme.

A second group included calculations with CNDO using a modified β (CNDO/M).

$$F_{\mu\nu} = {}^1/_2(\epsilon_\mu + \epsilon_\nu)S_{\mu\nu} - {}^1/_4(Z_A/n_A + Z_B/n_B)S_{\mu\nu}\gamma_{AB} - D_{\mu\nu} - {}^1/_2 P_{\mu\nu}{}^{C}\gamma_{AB} \qquad (20)$$

(Z/n is the average charge per orbital for a neutral molecule, *e.g.*, = 1 for H and C). All except the last element were lumped into $H_{\mu\nu}$ in order to preserve balance in the method. This term could be considered to be what CNDO/2 approximates by the use of

$$F_{\mu\nu} = \beta_{\mu\nu}S_{\mu\nu} - {}^1/_2 P_{\mu\nu}{}^{C}\gamma_{AB} \qquad (21)$$

since from eq 12, for a neutral molecule with one electron in each AO, the off-diagonal terms are

$$F_{\mu\nu} = {}^1/_2 S_{\mu\nu}(\epsilon_\mu + \epsilon_\nu) - G_{\mu\nu}{}^{R} \qquad (22)$$

The leading terms of these residual repulsion integrals are approximately

$$G_{\mu\nu}{}^{R} \approx {}^1/_4(q_\mu + q_\nu)S_{\mu\nu}\gamma_{AB} + {}^1/_2 P_{\mu\nu}\gamma_{AB} \qquad (23)$$

The primary reason for the intermediate stage of the CNDO/M calculations was to ensure that parameter changes alone were not responsible for the change in results on going from CNDO/2 to the Mulliken method. In fact the constant of 0.85 in the $D_{\mu\nu}$ expression was actually derived from setting the reaction energy for the ethylene + ethylene reaction equal in the CNDO/M and the CNDO/2 calculations (*vide infra*).

The third and fourth groups of calculations used a Mulliken evaluation of all of the repulsion integrals and attraction integrals using s orbitals. In the third case, $V_{AB} = Z_B\gamma_{AB}$, and in the fourth, $V_{AB} = Z_B(S|1/r_B|S)$ were used. The off-diagonal elements were taken as

$$F_{\mu\nu} = {}^1/_2(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu} + G_{\mu\nu} - D_{\mu\nu} \qquad (24)$$

Discussion

The particular dissection of the CNDO/2 method as given above as compared to some alternate dissective paths which might be taken does involve the assumption that charges by both CNDO/2 and Mulliken methods are approximately equal. This approximation, however, should not have a strong effect on the main energy terms since there is a net conservation of charge and thus deviations in charge will tend to produce energy terms which are at least partially canceling.

Table III summarizes energy results for four molecules by the CNDO/2 method as well as the similarly parametrized Mulliken methods. There are a number of striking results. First, the total energies vary widely. Second, the main part of the energy as given by eq 14 and 15 is about equal when the parameters determining that part of the energy are not changed. Thus there appears to be some validity to setting charges equal. Further, the change in V produces a significant change in the energy, but it appears to have little effect on relative energies. In addition, the energies due to $G_{\mu\nu}{}^{R}$ and $D_{\mu\nu}$, while small, are not insignificant. Change of the 0.85 coefficient in $D_{\mu\nu}$ alone, incidentally, does not qualitatively alter the results.

The CNDO/2 method makes many predictions which are not borne out in fact. Scaling of different types of interactions incorrectly is one of the most important.[10] The reasons for this can be seen from the equations and Table III. The basic energy terms of the Mulliken and CNDO methods are the same, but CNDO in effect replaces the correct V, $G_{\mu\nu}{}^{R}$, and $D_{\mu\nu}$ terms by a large β term. The energies derived from these terms appear to be either relatively insensitive to bonding or relatively

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(8) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

(9) Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.

(10) A. Streitwieser, Jr., and R. G. Jesaitis in ref 2a, p 197.

Table III. Energy Terms in MO Approaches[a]

Molecule	CNDO[b] diagonal	Mulliken[c,d] main	Mulliken[c,e] main	$G_{\mu\nu}{}^{R\,d}$	$G_{\mu\nu}{}^{R\,e}$	$D_{\mu\nu}{}^{d}$	$D_{\mu\nu}{}^{e}$	CNDO off[f] diagonal
Acetylene	280.992	288.305	334.650	27.111	27.133	15.680	15.702	136.395
Ethane	320.229	325.616	383.656	41.335	41.500	27.760	27.734	191.260
Total	601.221	613.921	718.306	68.446	68.633	43.440	43.436	327.655
Ethylenes (2)	603.330	616.476	719.414	68.274	68.346	42.576	42.596	325.284
Cyclobutane	602.197	616.957	721.150	68.106	68.180	41.083	41.076	341.556

[a] Each column represents the total energy due to the particular terms. [b] Equation 14, including core repulsion. [c] Equation 15, including core repulsion. [d] $V_{AB} = Z_B\gamma_{AB}$. [e] $V_{AB} = Z_B(S|1/r_B|S)$ (A $\neq$ B). [f] Equation 16.

small, whereas the β term contributes in a direct and large way to bond energy. Thus, when one compares the relative weights of say a "charge" interaction and a "resonance" interaction, one finds that the charge-energy-derived terms are weighted much differently from the bond-energy-derived terms. It is also not unreasonable that charged compounds do not seem to be handled correctly.[10-12] The latter is also possibly due to the neglect of charge differential terms in β. Poor treatment of strained compounds is also evident,[11,12] possibly because of incorrect scaling but also possibly due to the use of an insufficient basis set. Compounds with lone pairs are probably also incorrectly treated.[12,13] This may, however, be due solely to the use of spherical repulsion integrals, as calculations using the Mulliken approach as depicted here, for example, do not predict the correct order for the acidities of the cycloalkanes.[12,14]

Some glaring examples of poor predictive power are the predicted reaction energies as given by CNDO, as exemplified by the 15-eV exothermicity of the ethylene + ethylene reaction to give cyclobutane and the endothermicity of the ethane + acetylene reaction to give two ethylene molecules. These systems were actually chosen for this study partly because of the problems inherent in them as pointed out in ref 15.[15] The problem of reaction energies and atomization energies by CNDO/2 is a general one and much effort has been spent to correct it.[2a,16] The solution of Wiberg, in fact, seems to be one of the better ones in that atomization energies are compensated by an empirically found factor and this seems to in effect be a compensation for the large energy value derived from the empirical β.

One fact that is implied in the above discussion is that charges are given well by CNDO/2. This appears to be reasonable since the terms determining the density matrix, coupled with the normalization conditions, seem to be good approximations to a Hartree–Fock matrix. Thus dipole moments and charge distributions may, in fact, be a more reliable use of CNDO/2 calculations as indeed they seem to be.

In obtaining these conjectures, it is necessary to show that results by the Mulliken method are not unreasonable with these parameters though they cannot be expected to be as good as with an optimally parametrized Mulliken method.

The Mulliken method improves both of these reaction energies, although agreement with experiment is still not good. These quantities are summarized in Table IV along with the energies of the reactant molecules. It can be pointed out that reaction energies of this type, with strained compounds, tend to be difficult to obtain even with *ab initio* methods. For example, Buenker, Peyerimhoff, and Whitten[17] found that with a limited basis set the reaction energy for the acetylene + ethane to two ethylenes reaction was 0.348 eV, which was quite good, but with an optimized set they obtained a value of 0.769 eV. Snyder and Basch found a value of 0.555 eV.[18]

Table IV. Total Energies (eV) by the MO Methods[a]

Molecule or reaction	CNDO/2	CNDO/M	Mulliken[b]	Expt
Ethane	511.688	560.123	452.890	
Acetylene	417.837	429.207	377.485	
Ethylene	464.308	494.455	415.178	
Ethane + acetyl· → 2ethyl·	−0.459	−0.420	−0.019	0.38
Cyclobutane	943.752	1004.426	830.406	
2Ethyl· → cyclobutane	15.135	15.516	0.050	0.70
Ethane barrier, kcal	2.17	2.47	1.80	2.80

[a] Calculated at experimental geometries. [b] $V_{AB} = Z_B(S|1/r_B|S)$.

The barrier to rotation in ethane does not vary greatly, but bond lengths are predicted to be substantially shorter (~10%) in the Mulliken method than in CNDO/2, somewhat reminiscent of the results by the CNDO/1 method. This is correctable by slight modification of the V_{AB} terms, but there does not seem to be other than an empirical justification for doing this so we have avoided making modifications at this stage.

The charges given by both methods are similar, although the H charges in the Mulliken method are somewhat more positive. Table V summarizes these.

Table V. Hydrogen Charges

Molecule	CNDO/2	CNDO/M	Mulliken[a]	Mulliken[b]
Methane	0.987	0.942		0.955
Ethane	0.998	0.955	0.932	0.958
Ethylene	0.985	0.962	0.917	0.926
Acetylene	0.937	0.947	0.851	0.860
Cyclobutane	1.005	0.988	0.942	0.953

[a] $V_{AB} = Z_B\gamma_{AB}$. [b] $V_{AB} = Z_B(S|1/r_B|S)$.

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Table VI. Ionization Potentials

Molecule	CNDO/2	CNDO/M	Mulliken[a]	Expt
Methane	t_2 19.74	t_2 20.30	t_2 17.50	t_2 13.06
Ethane	e_g 16.37	e_g 16.14	a_{1g} 15.39	e_g, a_{1g} 10.7
Ethylene	σ 15.79	π 14.62	π 15.05	π 10.5
Acetylene	π 17.54	π 16.01	π 15.73	π 11.4

[a] $V_{AB} = Z_B(S|1/r_B|S)$.

Ionization potentials by Koopmans' theorem also do not differ greatly, although orbital structure is changed somewhat. These results are summarized in Table VI.

Conclusions

The nature of the CNDO approximations and the similarity of CNDO to the Mulliken method lead us to believe that Mulliken methods should be given serious consideration as alternatives to the CNDO/2 method. While the nature of the results does not point to a large improvement in predictive power by the Mulliken method as we have depicted it, it is probable that with reparametrization this should be possible. Many of the smaller terms neglected by the CNDO method are included in the Mulliken method although in an approximate way, so one does expect the Mulliken method should be somewhat more accurate.

If ZDO methods are to be used, it seems necessary to use parameters expressly derived for them, although some of the parameter sets now in use for CNDO methods might, in fact, turn out to be circumventions of the CNDO deficiencies rather than true ZDO parameters.

All of the terms which are included in the NDDO method but not included in CNDO are also not included in the Mulliken method.[2a] This implies that it should be possible to include these terms within a Mulliken framework and hence improve on simple Mulliken results.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. I. The Exchange of Enol Acetates with Acetic Acid Catalyzed by Palladium(II) Chloride[1]

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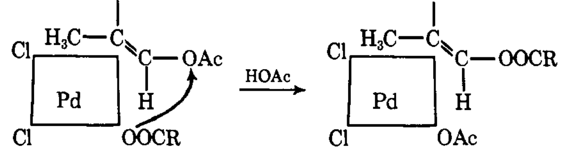
Abstract: The main Pd(II)-catalyzed exchange of $CH_2{=}CHOOCCD_3$ with CH_3COOH was found to obey the following rate expression: $-d[C_2H_3OOCCD_3]/dt = ([Li_2Pd_2Cl_6][C_2H_3OOCCD_3]/[LiCl])(k_1 + k_2[LiOAc])$. There may be a small contribution from a reaction with a higher LiCl inhibition. A study of the rates of isomerization and vinyl ester exchange of *cis*- and *trans*-1-acetoxy-1-propene showed that exchange occurs only with isomerization. The kinetics and stereochemical results are consistent with an oxypalladation–deoxypalladation mechanism for exchange: $C_2H_3OOCCD_3 + {\geqslant}PdOOCCH_3 \rightarrow {\geqslant}PdCH_2CH(OOCCD_3)(OOCCH_3) \rightarrow {\geqslant}PdOOCCD_3 + C_2H_3OOCCH_3$. This mechanism predicts that cyclic enol acetates should not exchange. It was found that 1-acetoxy-1-cyclopentene in fact did not exchange. Substitution on vinyl carbon strongly inhibits exchange. The relative rates for vinyl acetate, *trans*-1-acetoxy-1-propene isopropenyl acetate, and *cis*-2-acetoxy-2-butene are $1:2.5 \times 10^{-2}:3.3 \times 10^{-3}:1.6 \times 10^{-6}$.

Most Pd(II) reactions with organic substrates are oxidative in nature, resulting in reduction of Pd(II) to Pd(0) and giving oxidized organic products.[2] However, there are some Pd(II) reactions, in which the oxidation state of the Pd(II) remains unchanged, which are thus truly catalytic. Kinetic studies of these nonoxidative reactions are not complicated by side effects of precipitated palladium metal or of oxidants added to reoxidize the Pd(0) to Pd(II). Thus, mechanistic studies of these reactions offer a good method of elucidating some aspects the mode of Pd(II) reaction with organic substrates. One class of these nonoxidative reactions is the Pd(II)-catalyzed exchange reactions of which the vinyl ester exchange is an example.[3] For instance, vinyl acetate, in the presence of Pd(II), exchanges with acids to make other vinyl esters.

$$CH_2{=}CHOAc + RCOOH \rightleftarrows CH_2{=}CHOOCR + AcOH \quad (1)$$

The two mechanisms proposed for vinyl ester exchange are (a) an SN2 attack of acetate on a Pd(II)–vinyl acetate π complex (eq 2), a mechanism suggested for other Pd(II)-catalyzed exchanges,[4] and (b) an oxypalladation–deoxypalladation mechanism[5] (eq 3,



(2)

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[1] (a) Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., Apr 1969; *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B15 (1969); (b) Address correspondence to author at 419 Nicholas Ave., Wilmington, Del. 19803.

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