Table IV. Electronic Spectral Characteristics of Some Butyrophenones Observed in Cyclohexane Solution and in Solid KBr Matrix

Ketone	n → π* λ_{max},[a] Å.	n → π* λ_{max},[b] Å.	π → π* λ_{max},[a] Å.	π → π* λ_{max},[b] Å.
Butyrophenone	3220	3100[c]	2770	2790
p-Amino			2950	3080
p-Methoxy	3200[c]	3160	2510	2640
p-Hydroxy			2710	2780
p-Chloro	3250			2500
p-Bromo	3230			2550

[a] In cyclohexane solution. [b] In KBr matrix. [c] Weak shoulder.

Table V. Quantum Yields of Butyrophenone Disappearance at 3130 Å. in a KBr Matrix at Various Pressures

Ketone	Pressure, atm.	Φ
Butyrophenone	10,800	0.005
	6,800	0.01
p-Amino	10,800	0.000
	6,800	0.000
p-Methoxy	10,800	0.000
	6,800	0.000
p-Hydroxy	10,800	0.000
	6,800	0.000
p-Chloro	10,800	0.001
	6,800	0.003

of the ketones are shifted to the red and the n,π* bands to the blue. These observations are in agreement with those of Leermakers,[26] who studied the electronic spectra of ketones in cyclohexane–silica gel matrix.

The quantum yields of the type-II process of some butyrophenones in KBr matrix are given in Table V. The results show that change of environment to a KBr matrix reduces the quantum efficiency of the unimolecular decomposition of an excited triplet butyrophenone. A possible explanation is the presence of external heavy atoms in the KBr matrix which influences the decay processes from the excited triplet state.[27] Furthermore, experiments also show that the

quantum yields decrease with pressure. This effect is perhaps not surprising, since most of the unimolecular decomposition requires that in the transition state, the bonds are stretched before they break, thus giving a greater transition-state volume and a negative pressure effect.

(26) P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, 87, 1620 (1965).

(27) S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, 42, 3060 (1965).

Ground States of Conjugated Molecules.
IV.   Estimation of Chemical Reactivity[1]

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The semiempirical SCF–MO method described in previous papers of this series[2–4] has been used to calculate localization energies for a number of positions in various aromatic hydrocarbons and the changes in resonance energy when analogous arylmethanes are converted to the corresponding carbanions or carbonium ions. The results are correlated with partial rate factors for substitution in the hydrocarbons, with the relative rates of deprotonation of the arylmethanes with base, and with relative rates of solvolysis for the arylmethyl chlorides.

Introduction

Most of the theoretical work that has been done so far on attempts to predict chemical reactivity has made use of the simple Hückel MO method,[5] or simple variants of it based on the use of perturbation theory.[5,6] This kind of approach has been quite successful in the case of hydrocarbons; however, it seems to become progressively less reliable for molecules containing increasing numbers of heteroatoms or heteroatomic substituents—a result which is not surprising in view of the known deficiencies of the Hückel method.[7]

Obviously it would be much better if some more refined and reliable approach could be used in such calculations, and the obvious first choice in this connection is the semiempirical SCF–MO method introduced by Pople.[8] However, attempts to use the Pople treatment in calculations of reactivity have been disappointing, and relatively little work has been done in this field.

(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-01.

(2) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, 42, 756 (1965).

(3) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 685 (1965).

(4) M. J. S. Dewar and G. J. Gleicher, *ibid.*, 87, 692 (1965).

(5) See A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(6) M. J. S. Dewar, *J. Am. Chem. Soc.*, 74, 3357 (1952).

(7) See, *e.g.*, M. J. S. Dewar, *Rev. Mod. Phys.*, 35, 586 (1963).

(8) J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953); A. Brickstock and J. A. Pople, *ibid.*, 50, 901 (1954).

The previous papers[2-4] of this series discussed the problem of calculating ground-state properties of molecules by the SCF–MO method. It was pointed out that previous treatments of this kind had been illogical in certain respects. The values of certain integrals, notably the one-electron resonance integrals, β, had been estimated from spectroscopic data rather than data for molecules in their ground states, and the core repulsion had been calculated using a potential different from that assumed in estimating the attraction between the electrons and the core. An appropriately modified version of the SCF–MO method gave astonishingly accurate values for the heats of formation of a wide range of conjugated hydrocarbons, and preliminary results suggest that it may prove equally successful for molecules containing heteroatoms.[9] We have therefore re-examined the problem of calculating chemical reactivity by the SCF–MO method; this paper describes calculations of this kind for certain basic reactions involving aromatic hydrocarbons.

Theoretical Approach[10]

Attempts to calculate chemical reactivity have followed two main lines. First, there have been numerous attempts to correlate chemical reactivity with various quantities[5] calculated for the reactants (charge density, bond order, free valence, self-polarizability, frontier electron density, superdelocalizability, etc.); secondly, there have been studies based on attempts to calculate differences in energy between the reactants and the transition state.

From the standpoint of current kinetic theory, only the second approach has any validity. Any treatment of reactivity that neglects the transition state is incorrect in principle, and the success of such treatments is due solely to fortuitous correspondences between the various quantities in question and the energy differences that in fact determine the rates of reaction. It is true that correlations of this kind might be used on an empirical basis if the necessary correspondences always held—but they do not. Exceptions can be found without difficulty in each case.

The transition-state approach suffers, however, from three main difficulties. First, there is the problem, at present insuperable, of estimating entropies of activation; secondly, there is the problem of predicting the geometry of the transition state; thirdly, there is the problem of calculating the energy of the transition state, even in some assumed geometry. (This last difficulty arises from the fact that no satisfactory theoretical methods are yet available for dealing with σ-bonds. In a conjugated molecule, the heat of formation can be written adequately as a sum of σ-bond energies, which depend only on the atoms bonded and the bond length, and the π-bond energies which can be calculated theoretically. Transition states, however, contain bonds which are neither "localized" nor of π-type; at present there are no valid methods available for calculating their contributions to the total energy of the system.)

The first of these difficulties restricts us to calculations of relative rates only, and then only on the assumption that the entropies of activation are the same throughout; the relative rates are then determined only by relative potential energies of activation. This assumption has been discussed extensively in recent years and need not be considered further here; as a rule it appears to be valid for any series of similar reactions carried out under similar conditions, provided that no specific effects, such as steric hindrance, are involved.

The second and third difficulties can be met by involving a principle first put forward by Evans and Polanyi[11] who observed that in many reactions there is a linear relation between the free energy of activation (ΔF^*) and the free energy of reaction (ΔF)

$$\Delta F^* = a + b\Delta F \qquad (1)$$

A very good example of this is provided by the Brønsted relation, where ΔF^* is the free energy of activation for an acid-catalyzed reaction, and ΔF the corresponding difference in free energy between the reactants and a corresponding system in which a proton has been transferred from the acid catalyst to the substrate. If such a relation holds, and if our assumption of a constant entropy of activation for a series of related reactions is correct, then there should be a similar linear relation between the potential energy of activation (ΔE^*) and a potential energy of reaction (ΔE)

$$\Delta E^* = a' + c\Delta E \qquad (2)$$

The rate constants k for such a series of reactions will then be given in terms of ΔE by

$$-RT \log k = A + c\Delta E \qquad (3)$$

where A is a constant at constant temperature. Equation 3 is the basis for the use of quantities such as localization energies as measures of reactivity.[5]

It should be added that Horiuti and Polanyi[12] and Bell[13] have explained the existence of this linear energy relation in terms of a conventional model involving the crossing of potential energy surfaces. This model also leads to several important and obvious deductions[14]; first, the value of c should in general tend to be less, the more exothermic the reaction; secondly, the value of c gives an indication of the nature of the transition state since low values of c indicate a structure close to that of the reactants, while a value of c close to unity indicates a structure similar to that of the products.[15]

If these arguments are correct, then a plot of $(-RT \log k)$ vs. ΔE should be a straight line of slope c; since ΔE is a difference in potential energy between normal molecules, we should be able to calculate it by the general kind of approach developed in parts I–III.[2-4] This approach must obviously be used with

(9) See M. J. S. Dewar, G. J. Gleicher, and B. Robinson, J. Am. Chem. Soc., 86, 5698 (1964).

(10) Although the problem of calculating chemical reactivity has received much attention during the past 3 decades, confusion still remains about the procedures that should be adopted. We have therefore thought it best to summarize our point of view in the hope that this may avoid ambiguity and help to clear up some present misconceptions.

(11) M. G. Evans and M. Polanyi, Trans. Faraday Soc., 32, 1340 (1936).

(12) J. Horiuti and M. Polanyi, Acta Physicochim. URSS, 2, 505 (1935).

(13) R. P. Bell, Proc. Roy. Soc. (London), A154, 414 (1936); see R. P. Bell, "Acid–Base Catalysis," Clarendon Press, Oxford, 1941.

(14) (a) Cf. M. J. S. Dewar, Discussions Faraday Soc., 2, 261 (1947); (b) "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

(15) This principle has been referred to as "Hammond's Postulate" (cf. G. S. Hammond, J. Am. Chem. Soc., 77, 334 (1955)), but, as indicated above, this term seems a misnomer.

Table I. Relative[a] Localization Energies for Electrophilic Substitution

	Compound	Position[b]	Hückel[c]	β and C-C bond length fixed		Self-consistent β and C-C bond length	
				PPP, e.v.	SPO, e.v.	PPP, e.v.	SPO, e.v.
1	Benzene	..	0.000	0.000	0.000	0.000	0.000
2	Naphthalene	1	−0.237	−0.907	−0.905	−0.778	−0.672
3	Naphthalene	2	−0.056	−0.498	−0.539	−0.566	−0.571
4	Phenanthrene	1	−0.218	−1.057	−1.058	−0.920	−0.848
5	Phenanthrene	2	−0.038	−0.653	−0.709	−0.764	−0.831
6	Phenanthrene	3	−0.082	−0.831	−0.885	−0.851	−0.850
7	Phenanthrene	4	−0.170	−0.881	−0.874	−0.806	−0.767
8	Phenanthrene	9	−0.237	−1.060	−1.066	−0.952	−0.882
9	Anthracene	1	−0.286	−1.304	−1.310	−1.186	−1.061
10	Anthracene	2	−0.136	−0.832	−0.891	−0.941	−0.943
11	Anthracene	9	−0.523	−1.870	−1.836	−1.585	−1.326
12	Anthanthrene	6	−0.608	−2.453	−2.392	−2.100	−1.800
13	Pyrene	1	−0.346	−1.635	−1.639	−1.465	−1.320
14	Perylene	3	−0.396	−1.886	−2.036	−1.717	−1.509
15	Chrysene	6	−0.285	−1.451	−1.475	−1.273	−1.138
16	Benzo[a]pyrene	6	−0.575	−2.273	−2.236	−1.906	−1.602
17	Coronene	..	−0.230	−1.430	−1.463	−1.379	−1.293
18	Triphenylene	1	−0.158	−0.962	−0.965	−0.908	−0.911
19	Triphenylene	2	−0.059	−0.849	−0.914	−0.935	−1.012
20	Biphenyl	2	−0.136	−0.199	−0.175	−0.689	−0.695
21	Biphenyl	4	−0.089	−0.198	−0.216	−0.813	−0.885

[a] Localization energy of benzene set equal to zero. [b] "Ring Index" numbering throughout. [c] From ref. 5; we have checked most of these values.

caution; for the Bell–Polanyi derivation of eq. 2 rests in the assumptions that there are no specific resonance interactions in the transition state, and that the potential energy surfaces are planar over a sufficient region to make c constant for the whole series of reactions we are considering. Thus α-chloro ketones react with nucleophiles with great ease because the corresponding SN2 transition state is stabilized[14b] by resonance interactions between the 2p-orbital of the carbon atom at the reaction center and the adjacent $+E$ carbonyl group, while in several cases[13] there are indications that c can change along a series of reactions if the over-all range of rate constants is large.

In selecting reactions for study, we were therefore guided by three considerations: first, the reactants and products needed to be free from conjugated heteroatoms, so that the techniques of parts I–III could be applied directly; secondly, the reactions needed to be ones that are thought not to involve any special resonance interactions in the transition state; thirdly, series of reactions were needed where adequate rate data were available. These considerations led us to discuss the following reactions: (a) electrophilic substitution of aromatic hydrocarbons; (b) radical substitution of aromatic hydrocarbons; (c) deprotonation of arylmethanes, $ArCH_3$ where ArH is an aromatic hydrocarbon, to the corresponding carbanions, $ArCH_2^-$; (d) limiting SN1 solvolyses of corresponding arylmethyl chlorides, $ArCH_2Cl$. The quantities ΔE are then the differences in potential energy (a, b) between an aromatic hydrocarbon and a corresponding arenonium ion or radical; (c) between $ArCH_3$ and $ArCH_2^-$; (d) between $ArCH_2Cl$ and $ArCH_2^+$. If we accept the localized bond model for "localized" σ-bonds, then it is easily seen that for each series of reactions

$$\Delta E = \text{constant} + \Delta E_\pi \qquad (4)$$

where ΔE_π is the π-energy of reaction, i.e., the dif-

ference in total π-bond energy between the reactants and products. Equation 3 can then be written

$$-RT \log k = A' + C\Delta E_\pi \qquad (5)$$

where A' is constant for a series of analogous reactions carried out under similar conditions.

In the case of aromatic substitution, this of course is a familiar relation; here ΔE_π is the so-called[5] "localization energy." A similar approach has also been used[5] in the case of the other two reactions, ΔE_π in each case being calculated by the Hückel method or the perturbational MO (PMO) method.[6]

We have now calculated ΔE_π by the following variants of the SCF–MO procedures developed in parts I–III.[2,3]

A. Here all bonds between pairs of conjugated carbon atoms are assumed to have a common "aromatic" length (1.40 Å.); the values for the integrals were those corresponding to the PPP set in part II.[3]

B. Similar to A, except that modified SPO values were used for the integrals; see part II.[3]

C. A PPP calculation made self-consistent for changes in bond length; a separate calculation of this kind was carried out for reactant and product. For details, see part II.[3]

D. Similar to C, but using the modified SPO values for integrals.

Full details of the computational procedures will be found in parts I[2] and II.[3]

Results and Discussion

1. Electrophilic Localization Energies. Localization energies for 21 nonequivalent positions in 12 alternant aromatic hydrocarbons undergoing electrophilic substitution were computed using the four SCF–MO methods described in the previous section. The compounds studied and the calculated localization energies are given in Table I. For purposes of comparison, localization energies calculated by the Hückel method are also given in Table I. To facilitate comparisons
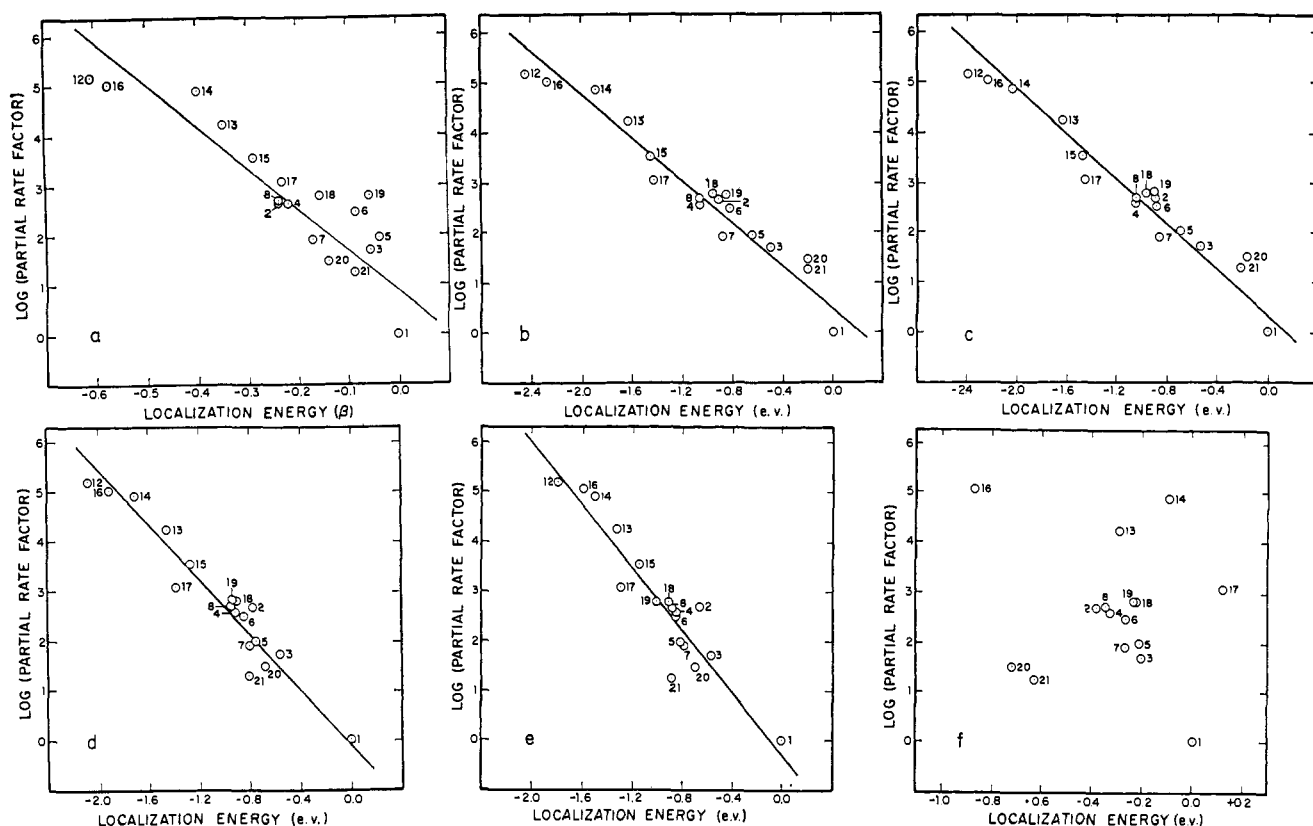
Figure 1. Relative electrophilic localization energies *vs.* logarithms of partial rate factors for nitration: (a) Hückel, (b) PPP with fixed β, (c) SPO with fixed β, (d) PPP with self-consistent β, (e) SPO with self-consistent β, (f) SPO with self-consistent parameters of parent hydrocarbons used for intermediates.

among the various methods as well as the different positions, the localization energy of benzene was set equal to zero and values for all other compounds were computed relative to this point. Thus, a negative localization energy is obtained for any compound which is more reactive than benzene.

As seen from Table I the four SCF methods give somewhat different values for the localization energies. The range of values is greatest for the PPP method with a fixed β (see part II[3]) and bond length (2.4525 e.v.), and smallest for the SPO method with self-consistent β and bond length (1.8000 e.v.). In order to examine the validity of the different methods, the calculated localization energies were plotted *vs.* experimental reactivities. In Figure 1a–f relative localization energies calculated by the Hückel and SCF methods are plotted against the logarithms of partial rate factors for nitration in acetic anhydride at 0°.[16] As Streitwieser[5] has pointed out, the Hückel results are essentially identical with those given by the simple perturbational method used by Dewar, Mole, and Warford[16] to interpret their data.

From Figure 1, it is seen that each of the SCF methods gives a better correlation with the experimental rate factors than does the Hückel method. It appears that the two techniques in which the C–C bond lengths and β values were fixed at a common value (Figure 1b and c) give slightly better correlations than the procedures allowing for variations in these terms.

(16) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

This behavior might have been due to the structures of the transition states in these reactions being much nearer to those of the reactants than to those of the products.

In the treatments allowing for variations in bond lengths, the lengths of the C–C bonds in the intermediate arenonium ion are frequently quite different from those in the original molecule. This is illustrated in Table II by data for the intermediate for α-substitution in naphthalene. We therefore calculated ΔE_π by an analogous procedure in which the bond lengths and $E_{\pi b}$ were estimated for the parent hydrocarbon, and the π-energy of the arenonium ion then found using the same values for the various integrals as in the final iteration for the parent hydrocarbon. This should correspond to a situation where the bond lengths do not vary during reaction, *i.e.*, to a model where the transition state resembles the reactants in geometry. In this case, however, there was no correlation at all between log k and ΔE_π (Figure 1f).

We think the errors in Figures 1d,e must be attributed to a weakness in our method for estimating bond lengths (part II[3]). Here we recalculate at each iteration all integrals for adjacent pairs of atoms; however, we do not recalculate integrals for more distant pairs. The resulting calculation does not therefore refer to a possible geometry for the molecule. Now the errors so introduced in the case of a neutral hydrocarbon are likely to be small, for the long-range interactions appear in the diagonal elements of the F-matrix only in terms of the form $(q_j - 1)(ii,jj)$—which vanish if atom j is neutral and so must be small in any neutral mole-
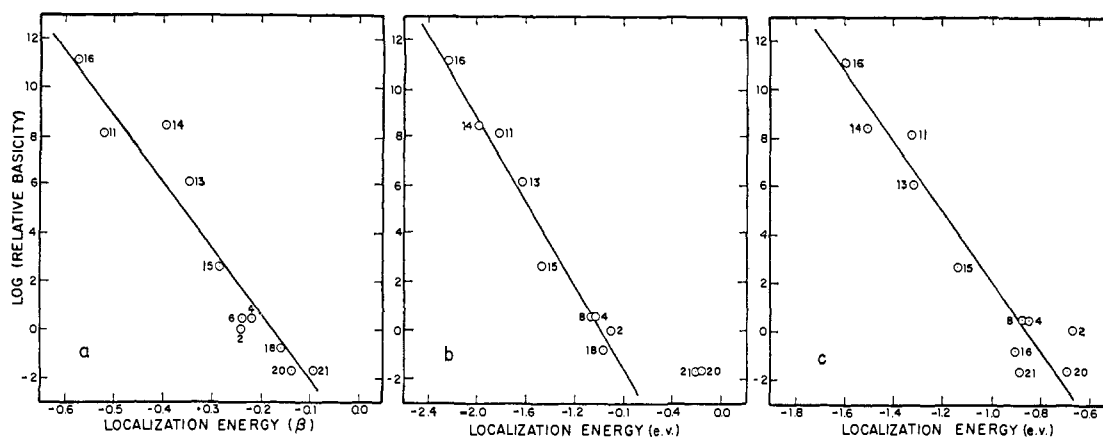
Figure 2. Relative electrophilic localization energies *vs.* logarithms of relative basicities: (a) Hückel, (b) SPO with fixed β, (c) SPO with self-consistent β.

cule—and in the off-diagonal elements in terms p_{ij}-(ii,jj)—which again are mostly small since bond orders between nonadjacent atoms are not normally large. However, the situation must be quite different in ions, where a number of charge densities q_j are likely to be very different from unity; the lack of self-consistency could then interfere with estimates of $E_{\pi b}$ from the arenonium ion.

Table II. Bond Lengths (Å.) for Naphthalene and Localized System with Atom in Position 1 Removed

Bond[a]	Obsd.[b]	PPP Naph-thalene	PPP Inter-mediate	SPO Naph-thalene	SPO Inter-mediate
1–2	1.363	1.378	...	1.374	...
2–3	1.415	1.419	1.369	1.425	1.366
3–4	1.363	1.378	1.422	1.374	1.428
4–10	1.421	1.424	1.408	1.429	1.406
5–10	1.421	1.424	1.422	1.429	1.424
5–6	1.363	1.378	1.390	1.374	1.389
6–7	1.415	1.419	1.402	1.425	1.402
7–8	1.363	1.378	1.406	1.374	1.409
8–9	1.421	1.424	1.386	1.429	1.383
9–10	1.418	1.407	1.424	1.400	1.427
1–9	1.421	1.424	...	1.429	...

[a] "Ring Index" numbering. [b] D. W. J. Cruikshank and R. A. Sparks, *Proc. Roy. Soc.* (London), A258, 270 (1960).

This argument suggests that it is essential to use a consistent set of bond lengths throughout the whole calculation; until the general problem of determining the whole geometry of the molecule as a function of individual bond lengths is solved (*cf.* part II[3]), it is probably better to assume all bonds between conjugated atoms equal rather than adopt half measures. This is an important conclusion, for it suggests that similar difficulties will arise in molecules containing heteroatoms. We are at present studying the extension of our SCF–MO treatment to such systems.

Chalvet, Daudel, and Kaufman[17] have recently reported SCF–MO calculations of localization energies in various aromatic hydrocarbons; comparison with their paper indicates that our results are in much better agreement with experiment than are theirs. The reason for this seems to lie in their neglect of core

repulsion. In their paper they plot log k against the difference in π-*binding* energy between reactants and intermediate arenonium ions, rather than the difference in π-*bond* energy (which is the quantity that appears in eq. 3). The π-bond energy, $E_{\pi b}$, of a molecule is given by

$$E_{\pi b} = E_\pi + E_{cr} \tag{6}$$

where E_π is the π-binding energy and E_{cr} the core repulsion. If the core repulsion were the same in the intermediate as in the parent hydrocarbon, then of course the procedure adopted by Chalvet, Daudel, and Kaufman would be satisfactory, but this is not the case. The π-system in the intermediate differs by one atom from that in the parent hydrocarbon, and so E_{cr} differs correspondingly. Indeed, the core repulsion is different for the intermediates corresponding to substitution at *different* positions in the *same* hydrocarbon; for this reason the procedure adapted by Chalvet, Daudel, and Kaufman does not even lead to a correct prediction of the relative proportions of isomers.

The quantity ΔE_π is the difference in π-energy between the parent hydrocarbon and the Wheland intermediate, or arenonium ion, for substitution at some position in it; ΔE_π can be related to the rate of substitution only by virtue of the free energy relationship between rates and free energies of reaction, and even then the results are uncertain by the scale factor embodied in eq. 3. If we had equilibrium constants (K) for the reversible formation of arenonium ions, this difficulty would not arise; for these should fit eq. 3 with $c = 1$. Now such data have been provided by Mackor and his collaborators[18] from studies of basicities of hydrocarbons, the conjugate acid of the hydrocarbon ArH being a corresponding arenonium ion ArH_2^+. Figure 2 shows plots of log K for protonation at various positions in a number of hydrocarbons against values of ΔE_π calculated (a) by the Hückel method, (b) by method B, and (c) by method D. (The plots for the PPP values, methods A and C, are omitted since they are not significantly different.)

In plot b, where ΔE_π is calculated assuming equal bond lengths, the points all lie close to a straight line, except those for biphenyl; however, the slope of the

(17) O. Chalvet, R. Daudel, and J. J. Kaufman, *J. Phys. Chem.*, **68**, 490 (1964).

(18) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

Table III. Relative[a] Localization Energies for Nucleophilic Substitution

	Compound	Position	β and C–C bond length fixed PPP, e.v.	SPO, e.v.	Self-consistent β and C–C bond length PPP, e.v.	SPO, e.v.
1	Benzene	..	0.000	0.000	0.000	0.000
2	Naphthalene	1	−0.915	−0.912	−0.786	−0.690
3	Naphthalene	2	−0.500	−0.544	−0.569	−0.569
4	Phenanthrene	1	−1.063	−1.072	−0.937	−0.888
5	Phenanthrene	2	−0.657	−0.720	−0.773	−0.853
6	Phenanthrene	3	−0.833	−0.889	−0.855	−0.859
7	Phenanthrene	4	−0.889	−0.898	−0.831	−0.829
8	Phenanthrene	9	−1.067	−1.081	−0.966	−0.913
9	Anthracene	1	−1.310	−1.328	−1.206	−1.112
10	Anthracene	2	−0.837	−0.906	−0.953	−0.975
11	Anthracene	9	−1.871	−1.835	−1.584	−1.320
12	Anthanthrene	6	−2.543	−2.499	−2.066	−1.770
13	Pyrene	1	−1.696	−1.709	−1.436	−1.287
14	Perylene	3	−1.227	−1.878	−1.707	−1.542
15	Chrysene	6	−1.521	−1.554	−1.239	−1.098
16	Benzo[a]pyrene	6	−2.276	−2.233	−1.909	−1.603
17	Coronene	..	−1.440	−1.484	−1.397	−1.330
18	Triphenylene	1	−0.973	−0.995	−0.939	−0.983
19	Triphenylene	2	−0.854	−0.925	−0.946	−1.039
20	Biphenyl	2	−0.212	−0.197	−0.709	−0.737
21	Biphenyl	4	−0.208	−0.231	−0.819	−0.899

[a] Localization energy of benzene set equal to zero.

line is only half what it should be, corresponding to $c = \frac{1}{2}$ in eq. 3. In the second plot the points show much more scatter; however, the points for biphenyl no longer deviate from the rest, and the slope of the line is now close to the theoretical one. Indeed, the difference (15%) is not significantly greater than the standard deviation in the slope of a line drawn through this somewhat scattered set of points.

These results suggest strongly that allowance must be made for variations in bond lengths in conjugated systems; by introducing an allowance for this, we not only bring the points for biphenyl into correspondence with the rest, but we also make the slope of the line close to the theoretical one. Of the compounds listed, biphenyl would suffer most from the unrealistic assumption of equal bond lengths, for the bond between the two rings in biphenyl is very much longer than the rest. Indeed physical measurements[19] indicate its length to be about 1.48 Å.

The scatter of the points in Figure 2b can again be attributed to the inadequacy of our method[3] for allowing for changes in bond length; clearly this is a problem that will have to be solved if the treatment is to be applied satisfactorily to ions or molecules containing heteroatoms. Two other factors that may have to be considered in a more refined treatment are the inductive effect, and possible hyperconjugative effects, of the saturated carbon atom in an arenonium ion on the adjacent unsaturated carbon atoms. A simple perturbation treatment[6] suggests that these effects would probably not affect the linear relation between rate or equilibrium constants and ΔE_π, but would reduce the value of c; the fact that c is close to unity for the "self-consistent" plot of Figure 2c suggests that these effects are probably relatively small.

One final point should be noted: the meaning of the term "localization energy." This has been used in two senses: (a) to denote the change in total π-bond energy when an atom in a conjugated system is attacked

(19) O. Bastiansen, Acta Chem. Scand., 3, 408 (1949).

by some reagent and so removed from conjugation with the rest; (b) to denote the change in the total π-electron energy of a conjugated system when two π-electrons are localized on one atom in it. Clearly it is the former quantity that is related to chemical reactivity; the second type of localization energy refers to an artificial state of a molecule and consequently is not an experimentally accessible quantity. This distinction did not matter in the Hückel treatment where both definitions are equivalent; however, this is not the case for localization energies calculated by the SCF–MO method. We therefore feel that the term should now be used only in the "chemical" sense of definition a.

2. Nucleophilic Aromatic Substitution. The simple Hückel method predicts[5] that there should be an exact correspondence between the relative rates of electrophilic substitution in aromatic hydrocarbons and the corresponding rates of radical or nucleophilic substitution. This prediction is supported qualitatively by the available evidence,[5,6] but as yet no quantitative data for nucleophilic substitution are available to test it. We wanted to see if a similar relation would hold for reactivities calculated by our SCF–MO method; we therefore calculated the values of ΔE_π listed in Table III. Figure 3 shows a plot of the values calculated by method B for electrophilic substitution against those for nucleophilic substitution; the points lie almost exactly in a straight line of unit slope, showing that the SCF method predicts correspondence between the two reactions similar to that given by the Hückel method. The values for ΔE_π given by A, C, and D show similar relationships.

3. Radical Aromatic Substitution. Localization energies for free-radical substitution computed by the four SCF methods are shown in Table IV. The range of values for radical localization energies is smaller by 0.4–0.6 e.v. than for electrophilic and nucleophilic substitution. For both the PPP and SPO methods

Table IV. Relative[a] Localization Energies for Radical Substitution

	Compound	Position	β and C–C bond length fixed		Self-consistent β and C–C bond length	
			PPP, e.v.	SPO. e.v.	PPP, e.v.	SPO, e.v.
1	Benzene	..	0.000	0.000	0.000	0.000
2	Naphthalene	1	−0.424	−0.452	−0.378	−0.256
3	Naphthalene	2	−0.161	−0.248	−0.227	−0.193
4	Phenanthrene	1	−0.372	−0.500	−0.349	−0.328
5	Phenanthrene	2	−0.137	−0.269	−0.218	−0.263
6	Phenanthrene	3	−0.193	−0.362	−0.252	−0.290
7	Phenanthrene	4	−0.282	−0.352	−0.329	−0.304
8	Phenanthrene	9	−0.460	−0.492	−0.467	−0.336
9	Anthracene	1	−0.650	−0.727	−0.650	−0.538
10	Anthracene	2	−0.374	−0.501	−0.502	−0.466
11	Anthracene	9	−1.003	−1.093	−0.939	−0.729
12	Anthanthrene	6	−1.460	−1.744	−1.213	−1.127
13	Pyrene	1	−0.793	−1.102	−0.616	−0.671
14	Perylene	3	−0.181	−1.136	−0.777	−0.742
15	Chrysene	6	−0.616	−0.779	−0.515	−0.419
16	Benzo[a]pyrene	6	−1.162	−1.425	−1.027	−0.922
17	Coronene	..	−0.507	−0.811	−0.587	−0.619
18	Triphenylene	1	−0.206	−0.325	−0.344	−0.165
19	Triphenylene	2	−0.091	−0.243	−0.282	+0.011
20	Biphenyl	2	+0.324	+0.283	−0.182	−0.148
21	Biphenyl	4	+0.363	+0.319	−0.236	+0.195

[a] Localization energy of benzene set equal to zero.

with fixed β and bond length, the localization energies for the 2- and 4-positions of biphenyl are greater than for benzene. For the SPO method with self-consistent β and bond length the values for 4-biphenyl are greater than for benzene. Also, the predicted reactivity for the 3-position of perylene is abnormally low by the PPP method with fixed parameters.
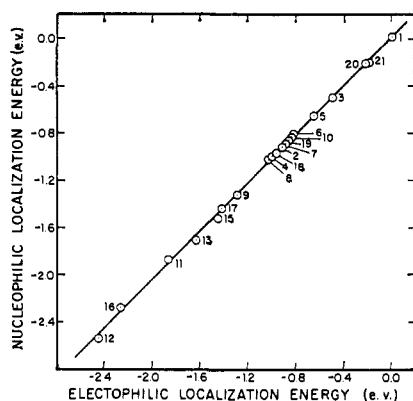
PPP and Hückel methods agree in predicting unit π-electron density at each position in the intermediate arenonium radical. It is therefore interesting to find that the "self-consistent" treatment of bond lengths (method D) this time gives a better correspondence with
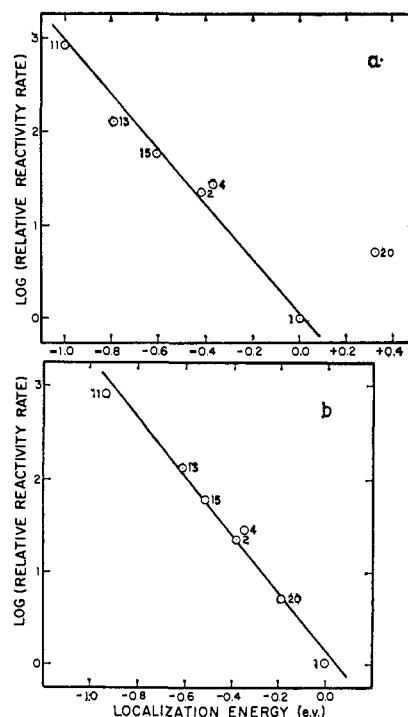

Figure 3. Relative electrophilic localization energies vs. relative nucleophilic localization energies by PPP method with fixed β.

To check the validity of these calculations, the localization energies were plotted against logarithms of partial rate factors for substitution by methyl,[20] trichloromethyl,[21] and trifluoromethyl[22] radicals. The plots for methylation vs. ΔE_π calculated by methods B and D are shown in Figure 4; the other plots were closely similar. In this case the intermediate is a neutral species rather than an ion; indeed, in the case of radical substitution in an alternant hydrocarbon, the

Figure 4. Relative radical localization energies vs. logarithms of relative reactivity rates for methyl radicals: (a) PPP with fixed β, (b) PPP with self-consistent β.

(20) M. Lay and M. Szwarc, J. Am. Chem. Soc., 77, 1949 (1955).
(21) E. C. Kooyman and E. Farenhorst, Trans. Faraday Soc., 49, 58 (1953).
(22) A. D. Stefani and M. Szwarc, J. Am. Chem. Soc., 84, 3661 (1962).

experiment than does method B; this supports strongly our suggestion that the deviations in the case of electrophilic substitution are due to our incomplete assessment of the effect of changing bond lengths, and that a
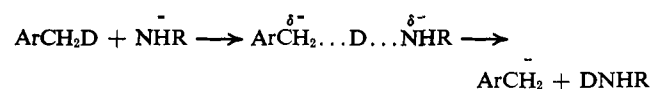
Table V. Relative[a] Energy Difference between Arylmethyl Anions and Parent Hydrocarbons

	Ar group	Position	Fixed β and C–C bond length PPP, e.v.	SPO, e.v.	Self-consistent β and C–C bond length PPP, e.v.	SPO, e.v.
1	Phenyl	..	0.000	0.000	0.000	0.000
2	Naphthyl	1	−0.527	−0.531	−0.442	−0.365
3	Naphthyl	2	−0.298	−0.313	−0.313	−0.308
4	Phenanthryl	1	−0.637	−0.651	−0.554	−0.515
5	Phenanthryl	2	−0.391	−0.420	−0.446	−0.496
6	Phenanthryl	3	−0.483	−0.511	−0.485	−0.486
7	Phenanthryl	9	−0.649	−0.652	−0.565	−0.518
8	Anthracyl	2	−0.518	−0.542	−0.542	−0.542
9	Anthracyl	9	−1.179	−1.192	−1.053	−0.884
10	Pyrenyl	1	−1.088	−1.123	−0.925	−0.853
11	Pyrenyl	2	−0.465	−0.489	−0.420	−0.486
12	Pyrenyl	4	−0.831	−0.833	−0.638	−0.599
13	Fluoranthyl	3	−1.164	−1.150	−1.169	−1.103
14	Fluoranthyl	8	−0.517	−0.557	−0.534	−0.577

[a] Energy difference for phenyl set equal to zero.

truly self-consistent treatment might be expected to give much better results.

4. Carbanion Reactions. Streitwieser and Langworthy[23] have studied the rates of dedeuteration of deuteriomethyl derivatives of aromatic hydrocarbons by lithium cyclohexylamide in cyclohexylamine. The reaction may be represented

$$ArCH_2\overset{-}{D} + N\overset{\delta^-}{H}R \longrightarrow Ar\overset{\delta^-}{C}H_2\ldots D\ldots\overset{\delta^-}{N}HR \longrightarrow$$

$$ArCH_2 + DNHR$$

If our assumption of a linear relation between free energies of activation and energies of reaction applies, then the rate constants for this reaction should follow eq. 5, ΔE_π now being the difference in π-energy between the parent aromatic system, ArH, and the anion $ArCH_2^-$.

Values for ΔE_π calculated by the four methods are listed in Table V, while Figure 5 shows plots of the logarithms of the relative rates of dedeuteration against the two sets of SPO values for ΔE_π. In each case the points lie close to a straight line, the standard deviations being comparable in each case.

Streitwieser and Langworthy tried to correlate their rate data with values of ΔE_π calculated by the Hückel method, but here a plot of log k vs. ΔE_π gave a scattered set of points. In order to extract any correlations from this, they had to assume that carbanions analogous to α-naphthylmethyl in geometry are sterically hindered by interactions between the methylene and peri hydrogen, so that the rates of reaction leading to them are systematically less than for unhindered ions such as β-naphthylmethyl. Most of the points for the two sets of compounds did indeed lie on two straight lines which were more or less parallel, as this explanation would require. However, two of the eleven compounds studied by them showed serious deviations; in the case of 3-methylfluoranthene this could have been due to experimental error, but in the case of 2-methylpyrene the deviation was clear.

Our results suggest that the distinction between "α-naphthyl" and "β-naphthyl" types may well have been an artifact of the method used to estimate ΔE_π;

the plots in Figure 5 show no distinction between the two types. In our case 2-methylpyrene behaves quite normally; Streitwieser and Langworthy guessed, apparently correctly, that the deviation in their plot might be due to neglect of long-range electronic repulsions in the simple Hückel treatment used by them to estimate ΔE_π.
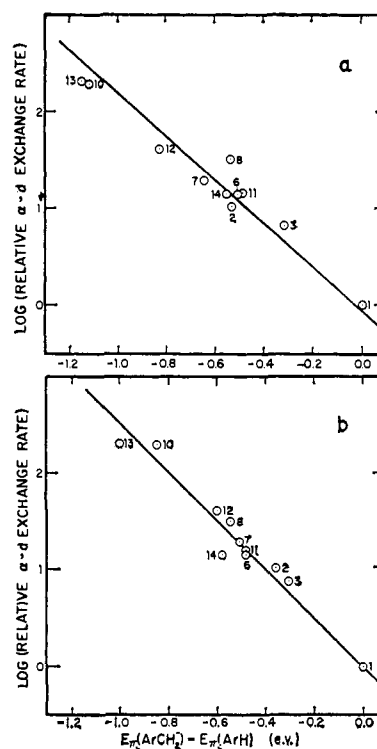
Figure 5. π-Energy differences between arylmethyl anions and parent hydrocarbons vs. logarithms of relative α-deuterium exchange rates: (a) SPO with fixed β, (b) SPO with self-consistent β.

5. Arylmethyl Cations. Dewar and Sampson[24] have reported measurements of the rates of solvolysis of a number of arylmethyl chlorides in moist formic acid. If this is a true "limiting" SN1 reaction, involving a free carbonium ion as intermediate, the rates would be

(23) A. Streitwieser and W. C. Langworthy, J. Am. Chem. Soc., 85, 1757, 1761 (1963).

(24) M. J. S. Dewar and R. J. Sampson, J. Chem. Soc., 2789 (1956); 2946 (1957).

Table VI. Relative[a] Energy Difference between Arylmethyl Cations and Parent Hydrocarbons

	Ar group	Position	Fixed β and C–C bond length PPP, e.v.	Fixed β and C–C bond length SPO, e.v.	Self-consistent β and C–C bond length PPP, e.v.	Self-consistent β and C–C bond length SPO, e.v.
1	Phenyl	..	0.000	0.000	0.000	0.000
2	Naphthyl	1	−0.525	−0.529	−0.435	−0.349
3	Naphthyl	2	−0.296	−0.304	−0.304	−0.283
4	Phenanthryl	1	−0.633	−0.643	−0.537	−0.480
5	Phenanthryl	2	−0.387	−0.403	−0.428	−0.451
6	Phenanthryl	3	−0.480	−0.501	−0.474	−0.461
7	Phenanthryl	4	−0.504	−0.497	−0.461	−0.429
8	Phenanthryl	9	−0.645	−0.642	−0.550	−0.482
9	Anthracyl	2	−0.512	−0.522	−0.519	−0.481
10	Anthracyl	9	−1.181	−1.203	−1.054	−0.894
11	Pyrenyl	1	−1.087	−1.126	−0.917	−0.847
12	Pyrenyl	2	−0.460	−0.469	−0.395	−0.427
13	Pyrenyl	4	−0.827	−0.822	−0.618	−0.551
14	Chrysyl	6	−0.966	−1.002	−0.745	−0.644
15	Triphenylyl	1	−0.561	−0.556	−0.535	−0.530
16	Triphenylyl	2	−0.498	−0.525	−0.537	−0.578
17	Fluoranthyl	3	−0.715	−0.761	−0.690	−0.673
18	Fluoranthyl	8	−0.636	−0.664	−0.606	−0.603

[a] Energy difference for phenyl set equal to zero.

expected to follow eq. 5, ΔE_π being the difference in π-energy between the parent hydrocarbon ArH and
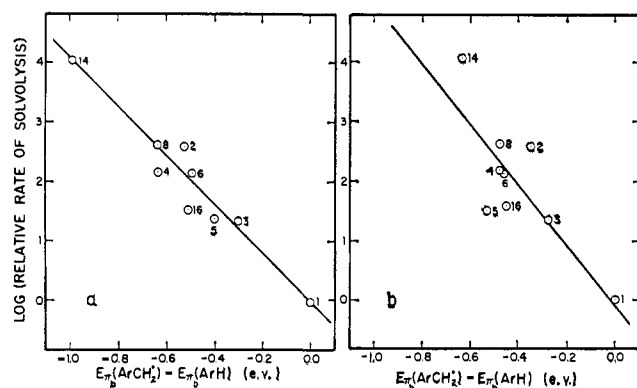

Figure 6. π-Energy differences between arylmethyl cations and parent hydrocarbons vs. logarithms of relative rates of solvolysis in moist formic acid: (a) SPO with fixed β, (b) SPO with self-consistent β.
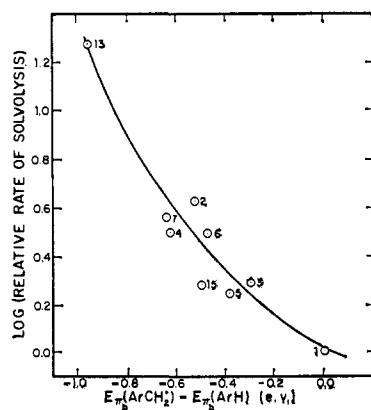

Figure 7. π-Energy differences between arylmethyl cations and parent hydrocarbons vs. logarithms of relative rates of solvolysis in 80% ethanol (SPO with fixed β).

the arylcarbonium ion, $ArCH_2^+$. Dewar and Sampson plotted logarithms of their rate constants against values for ΔE_π calculated by the simple PMO (per-

turbational MO) method; as in the case of the carbanions, the points lay on not one but two distinct straight lines, corresponding to chlorides of "α-naphthyl" or "β-naphthyl" type.
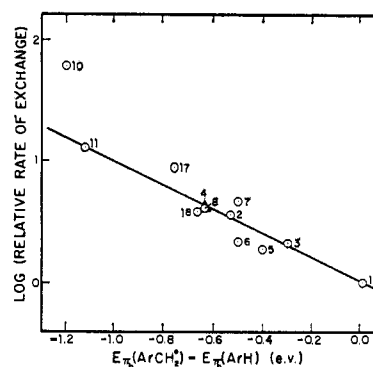

Figure 8. π-Energy differences between arylmethyl cations and parent hydrocarbons vs. logarithms of relative exchange rates with iodide ion in acetone (SPO method with fixed β).

Dewar and Sampson noted that similar linear relations exist for three other reactions of the same arylmethyl chlorides; solvolysis in a ternary mixture of formic acid, dioxane, and water, solvolysis in aqueous ethanol, and replacement of chlorine by iodine by reaction with iodide ion in acetone. The slopes of the plots of log k vs. ΔE_π, and the difference between the two sets of chlorides, changed systematically along this series of reactions; Dewar and Sampson interpreted this in terms of a continuous change in reaction mechanism from limiting SN1 (solvolysis in formic acid) to pure SN2 (reaction with iodide ion in acetone).

Table VI shows values for ΔE_π calculated by our four SCF methods, and Figure 6 shows plots of the logarithms of the rate constants (k) against the two sets of SPO values for ΔE_π. As in the case of electrophilic substitution, the points for ΔE_π calculated with fixed β values give quite a good linear correlation with log k, while those for ΔE_π calculated with self-consistent β values show more scatter. Here again the SCF

calculations draw no distinction between chlorides of "α-naphthyl" or "β-naphthyl" type.

Figures 7 and 8 show plots of ΔE_π (fixed β) vs. log k for solvolysis of chlorides in 80% ethanol, and for their SN2 reactions with iodide ion in acetone, respectively. The points for the SN2 reaction lie fairly close to a straight line, with the exception of 9-chloromethylanthracene; the anomalously high reactivity of this could be a steric effect, it alone having no free position *ortho* to the chloromethyl group. The points in Figure 7 do not lie on a straight line, but a smooth curve can be drawn that passes close to them; Dewar and Sampson[24] obtained similar curved plots for solvolysis of these chlorides in certain mixed solvents and pointed out that this could be explained very reasonably in terms of a change in structure of the transition state, this resembling a carbonium ion more closely in the case of the more reactive chlorides. As was pointed out in the sections on electrophilic substitution, the residual scatter in these plots may well be due to our failure to allow for variations in bond length; we hope soon to be able to modify our procedure so as to calculate the whole molecular geometry in a self-consistent manner.

Kinetics of the Thallic Ion Oxidation of Olefins.
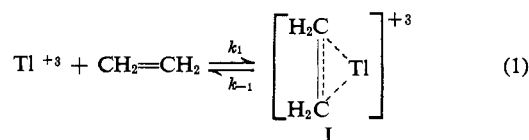## II. Effect of Olefin Structure on Rate and Product Distribution

Patrick M. Henry

Contribution from the Research Center, Hercules Powder Company, Wilmington, Delaware 19899. Received April 30, 1965

The oxidation of ethylene, propylene, and the four butenes by aqueous thallic ion was found to give saturated carbonyl products and glycols as primary oxidation products. The reaction was first order in olefin and first order in thallic ion and not retarded by acid. The effect of structure on rate was analogous to that found for the hydration of olefins. Based on the kinetics and rate effects, a reaction scheme proceeding through an oxythallation adduct, in which the formation of the oxythallation adduct is rate determining, is proposed. The activated complex for oxythallation must have considerably more carbonium ion character than that for oxymercuration. The effect of olefin structure on product distribution is that expected if the products arise by decomposition of the oxythallation adducts postulated as intermediates, assuming thallium(I) behaves as a normal leaving group.
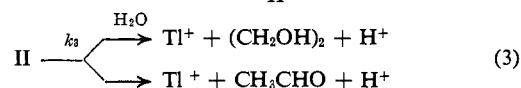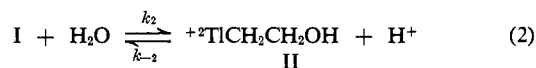
Introduction

Aqueous thallic ion oxidizes olefins to mixtures of glycols and carbonyl compounds.[1] In the first paper of this series,[2] the oxidation of ethylene to a mixture of acetaldehyde and ethylene glycol was found to be first order in thallic ion, first order in ethylene, not retarded by acid, and strongly accelerated by increasing salt concentration. On the basis of these results, plus supporting evidence, the following reaction scheme was proposed

$$Tl^{+3} + CH_2=CH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{bmatrix} H_2C \\ \vdots \\ H_2C \end{bmatrix}^{+3} Tl \quad (1)$$

(1) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).
(2) P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990 (1965).

$$I + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} {}^{+2}TlCH_2CH_2OH + H^+ \quad (2)$$
$$II$$

$$II \xrightarrow{k_3} \begin{cases} Tl^+ + (CH_2OH)_2 + H^+ \\ Tl^+ + CH_3CHO + H^+ \end{cases} \quad (3)$$

where k_1 or k_2 must be rate determining, since the reaction displays no proton inhibition. The effect of olefin structure on rates and distribution of products would depend greatly on the nature of the rate-determining step as well as the mode of decomposition of II. Therefore, to gain further insight into the mechanism of the reaction, the oxidation of propylene and the four butenes was studied.

Results

Kinetics. The reaction was studied in aqueous perchloric acid. All rates were measured by olefin uptake at olefin pressures of 1 atm. or less. During the course of a run, the olefin pressure was almost constant.

The rates of the oxidation of the substituted ethylenes were much faster than the rate for ethylene itself. To avoid mass transfer control of rate, the reaction was studied in a reactor of high gas–liquid mixing efficiency. Experimentally determined mass transfer coefficients were used to choose reaction conditions such that the rate constants measured were almost free of errors resulting from mass transfer control.

The reaction could be shown to be first order in thallic ion by plotting the data for a given run as described previously.[2] The reaction was found to be first order in olefin concentration for all olefins studied by measuring the pseudo-first-order rate constant at several different olefin pressures.

The values of the experimental second-order rate constants, k', are listed in Table I for three different acid concentrations.