Iron and Chromium Tricarbonyl Derivatives of Unsaturated Hydrocarbons

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Abstract: It is found that experimental data on iron tricarbonyl derivatives of unsaturated hydrocarbons can be satisfactorily explained by a localization energy approximation of the Hückel type which describes the ease with which a "butadiene unit" can be partially isolated from the hydrocarbon. The approach can be used to predict future compounds and should be a guide to further experimental work; several specific forecasts are made, including suggestions for the isolation of unstable hydrocarbons. A similar approach is helpful in understanding the chemistry of chromium tricarbonyl derivatives of benzenoid hydrocarbons. Particularly satisfactory is the correlation of the contrasting properties of iron and chromium tricarbonyl derivatives of polyacenes.

Many complexes of iron carbonyls with unsaturated hydrocarbons are now known; the most common type has an iron tricarbonyl ($Fe(CO)_3$) group bonded to a "butadiene unit" of the hydrocarbon.[1] There has been dispute about the details of the bonding,[1] with two extreme views: either that all the butadiene carbons are sp^2-hybridized and the whole butadiene unit is π-bonded to the metal; or that the two terminal carbons are sp^3-hybridized and form metal–carbon σ bonds, with π bonding between the metal and the two central carbons. Recent molecular orbital descriptions[2,3] have clarified the issue: if it is remembered that the stablest antibonding orbital of butadiene can accept electrons from the metal, the π-bonded model becomes compatible with the evidence which was formerly thought to imply σ bonding; the argument is really about the extent of the electron donation from the metal to this ligand orbital. To throw more light on these interesting compounds we have investigated theoretically the experimental data[1,4–9] on $Fe(CO)_3$ derivatives. Our objects are to explain why some hydrocarbons react more easily than others, why $Fe(CO)_3$ prefers one butadiene unit to another when there is a choice, and why for some hydrocarbons compounds have been isolated with two $Fe(CO)_3$ groups but not with one. We shall also consider similar questions for compounds where chromium tricarbonyl ($Cr(CO)_3$) is bonded to a benzenoid ring of an unsaturated hydrocarbon.

Theoretical Approach

General. Hückel molecular orbital theory is often helpful in correlating the rates of reaction of different unsaturated hydrocarbons. Many reactivity indexes have been proposed;[10–12] in particular, localization energies have been successfully used to discuss reactions such as aromatic substitution, Diels–Alder addition, and the reaction of osmium tetroxide (OsO_4) with a double bond.[10–12] A model of the hydrocarbon in the transition state is assumed, in which the appropriate carbon $2p\pi$ orbitals have been completely removed, or localized, from the delocalized π system; the resonance integrals of all the bonds involving these orbitals are put equal to zero. The π-localization energy (the decrease in delocalization energy incurred in going from the unperturbed hydrocarbon to the transition state) is then calculated. The lower this localization energy, the more readily the hydrocarbon is expected to react.

The theoretical justification and relative merits of the various Hückel reactivity indexes have been much discussed;[10–12] localization energies are perhaps the most fundamental.[13] We shall restrict ourselves to a few comments particularly relevant to the present application.

The use of a localization energy index is most easily justified if the transition state is a completely localized σ complex, with sp^3 hybridization at the appropriate carbons. The relative rates of reaction of different hydrocarbons with a given incoming group will then be determined mainly by the π-localization energy; other contributions to the activation free energy, such as solvation energies, entropies of activation, and changes in the σ framework (in particular the formation of the new σ bonds), will probably be fairly constant. It should be realized that it is not necessary to assume that the resonance integrals between a newly formed carbon sp^3 hybrid and the neighboring $2p\pi$ orbitals are zero. They will certainly be less than the unperturbed $2p\pi$–$2p\pi$ resonance integral β, partly because of the lengthening of the carbon–carbon bonds, but they will not be insignificant. The real point is that the sp^3 hybrid is now involved in a σ bond, which the original $2p\pi$ orbital was not; the electrons in this σ bond cannot contribute to the π-delocalization energy except *via* hyperconjugation. This effect can

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(1) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964), and references therein.

(2) M. R. Churchill, *J. Organometal. Chem.* (Amsterdam), **4**, 258 (1965).

(3) S. F. A. Kettle and R. Mason, *ibid.*, **5**, 97 (1966).

(4) T. A. Manuel, *Inorg. Chem.*, **3**, 1794 (1964).

(5) T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3597 (1961).

(6) R. B. King and F. G. A. Stone, *ibid.*, **82**, 4557 (1960).

(7) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

(8) T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

(9) E. H. Braye and W. Hübel, *J. Organometal. Chem.* (Amsterdam), **3**, 38 (1965).

(10) (a) R. D. Brown, *J. Chem. Soc.*, 691 (1950); (b) *ibid.*, 2730 (1950); (c) *ibid.*, 3249 (1950); (d) *ibid.*, 1950 (1951); (e) *ibid.*, 3129 (1951); (f) *Quart. Rev.* (London), **6**, 63 (1952); (g) in "Moleclar Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin, Ed., Academic Press, Inc., New York, N. Y., 1964, p 485.

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

(12) K. Fukui in ref 10g, p 513.

(13) Reference 11, p 341.

be simulated by putting the resonance integrals equal to zero. It has been found that explicit inclusion of hyperconjugation does not alter conclusions based on π-localization energies.[13]

In fact, the transition state is usually not a completely localized σ complex. For Diels–Alder addition only the final adduct is completely localized. Even for aromatic substitution semiquantitative correlations often require a value of β as small as -10 kcal, indicating that the transition state is only partially localized.[12,14]

To deal with this situation a number of reactivity indexes have been defined in terms of small perturbations to the isolated hydrocarbon.[11,12] Fortunately, these indexes accord closely with each other and with localization energies in their predictions of relative rates of reaction;[10d,e,11,12] for alternant hydrocarbons the interdependence of the various indexes can be proved mathematically.[11,12] Of particular interest is the π-extension model.[15] In this approach the $2p\pi$ orbital at the reaction center is not removed from the π system by the incoming group; instead it is assumed that the incoming group provides an orbital which by σ overlap with the unchanged $2p\pi$ orbital effectively extends the π system. At first sight this may seem the opposite extreme to a completely localized model; in fact, the two descriptions are inextricably interrelated. The smaller the loss of delocalization energy when a given carbon is localized from the π system, the greater will be the gain in σ-bond energy when the same carbon, still in the π system, begins to form a bond to an attacking group.[15] It is because of this connection that localization energy indexes can be used irrespective of the degree of localization in the transition state.

A more accurate estimate of the interaction between the π system and the incoming group could be obtained from a full molecular orbital discussion. In perturbation treatments along these lines,[11,12] some or all of the interactions between the molecular orbitals of the hydrocarbon and of the attacking group are allowed for individually. Again these approaches are usually equivalent to the use of localization energies,[11,12] and no better despite additional parameters.[11] One point can be seen clearly from the more elaborate expressions:[12] at least for alternant hydrocarbons explicit consideration of back-donation from filled orbitals of the incoming group to empty orbitals of the hydrocarbon is unnecessary; it would merely reinforce conclusions based on more conventional approaches.

Application to Metal Carbonyl Derivatives. We can now discuss the formation of $Fe(CO)_3$ and $Cr(CO)_3$ derivatives of unsaturated hydrocarbons. There has been little work on the kinetics of these reactions, though there has been some recent work on the formation of molybdenum tricarbonyl derivatives from hydrocarbons and molybdenum hexacarbonyl.[16,17] A complicated system of equilibria was suggested.[17] A similar situation probably holds for $Cr(CO)_3$ derivatives, some of which as we shall see later are unstable.

For the moment we shall consider only $Fe(CO)_3$ derivatives. These compounds are stable once prepared but their preparation often presents difficulties;[4] if no reaction occurs this is most naturally interpreted as a comment on the rate of reaction rather than on the equilibrium constant. Similarly the isolation of a compound with $Fe(CO)_3$ bonded to one part of the hydrocarbon rather than another is a reflection on the relative rates of reaction at the two sites, provided that $Fe(CO)_3$ cannot move freely about the molecule once a complex has been formed; such movement is indeed restricted, except between equivalent butadiene units as in cyclooctatetraene, as we shall note later. In any case, insofar as the bonding in the transition state relates to the bonding in the final complex, it is to be expected (with the reservation mentioned below) that the site which reacts most readily will also lead to the most stable compound.[10a,c] Thus, for Diels–Alder addition both reaction rates and equilibrium constants have been correlated by localization energies.[11]

We shall assume that the rate of formation of $Fe(CO)_3$ derivatives is determined by the interaction of $Fe(CO)_3$ with a butadiene unit, and that this interaction can be discussed in terms of localization energies. The choice of justifications is as above: the more easily the butadiene unit can be localized the more effectively it can interact with the incoming group, and the less it matters that the butadiene unit is to some extent bonded to the metal rather than involved in the π system of the hydrocarbon. In view of the success we shall have with this simple approach and the qualitative nature of the experimental data, there is no warrant for a more elaborate molecular orbital treatment. (The possibility was considered that the energies or coefficients of the highest occupied and lowest vacant molecular orbitals of the hydrocarbon might decide the rate of reaction, but no such correlation could be established.)

It should be clear from the earlier remarks that though the localization energy is calculated by reducing the appropriate resonance integrals, this need not imply that these resonance integrals are actually reduced during reaction. The previous arguments for the use of localization energies hold just as well if the resonance integrals are unchanged. This point is important for the present application. The structural changes in the butadiene unit when $Fe(CO)_3$ is added (a shortening of the central bond and a tendency to sp^3 hybridization at the terminal carbons[1–3,18–21]) suggest that while the resonance integrals for carbon–carbon bonds involving the terminal carbons may be slightly reduced, that for the central bond may be slightly increased. We shall not need to allow for these alterations, which are less important than the localization energy itself.

We must now decide what model of the transition state should be used in calculating localization energies. First we can rule out models which involve the localization of only two (or one, or three) of the four butadiene

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(14) Reference 11, p 401.

(15) Reference 11, p 403.

(16) D. A. Brown, N. J. Gogan, and H. Sloan, *J. Chem. Soc.*, 6873 (1965).

(17) H. Werner and R. Prinz, *J. Organometal. Chem.* (Amsterdam), **5**, 79 (1966).

(18) (a) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 421 (1960); (b) *Acta Cryst.*, **16**, 758 (1963).

(19) R. P. Dodge, *J. Am. Chem. Soc.*, **86**, 5429 (1964).

(20) D. J. Smith and L. F. Dahl, *ibid.*, **84**, 1743 (1962).

(21) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

carbons, such as a Diels–Alder model in which only the two terminal carbons are removed from the π system. They all fail to explain the experimental results (for example, to anticipate the later discussion, a Diels–Alder model wrongly predicts that $Fe(CO)_3$ should add to the central rather than to a terminal ring of anthracene). This indicates that, as expected, all four carbons must be involved in the rate-determining step.

The most obvious model might seem to be to remove all four butadiene carbons completely from the delocalized system of the hydrocarbon. However, this approach also fails to correlate the experimental data (to anticipate again, it wrongly predicts that 1-vinylnaphthalene and the divinylbenzenes should react less readily than naphthalene and anthracene). It is in any case unsatisfactory for other reasons. Complete localization of the butadiene unit does not provide a reasonable description of an $Fe(CO)_3$ derivative; spectral data[1,22] show clearly that the comparatively weak iron–carbon bonding does not perturb the unsaturated system so drastically even in the final compound, let alone the transition state. A partially localized model is more appropriate.

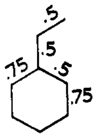
It is here that we find an important difference from previous localization energy treatments. In the past it has always been assumed that the degree of localization is merely a scale factor, which does not alter qualitative predictions of relative rates of reaction. Localization energies are calculated from a completely localized model; partial localization merely necessitates the use of a smaller value for β. This is quite satisfactory when only isolated carbons are involved, as in aromatic substitution or the Diels–Alder reaction. But it is not acceptable when adjacent carbons are being localized, as in $Fe(CO)_3$ derivatives. In a partially localized model the carbon–carbon bonds which involve only one carbon of the butadiene unit will be less affected than the three carbon–carbon bonds within the butadiene unit, whereas all these bonds will be equally affected, with resonance integrals reduced to zero, if the butadiene unit is completely removed. There is thus a difference other than of scale between the models; they can, and do, lead to different predictions. One consequence is that the $Fe(CO)_3$ derivatives which are formed most readily may not always be the most stable.

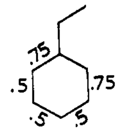
The earlier conclusion that the use of localization energies is appropriate irrespective of the degree of localization still holds in principle. But the correct localization energy for a given reaction is a partial localization energy calculated with reference to the degree of localization obtaining in the transition state. In discussing the localization of butadiene units this complication can no longer be ignored.

The only remaining question is whether or not all four butadiene carbons should be localized to the same extent in a partially localized model. We shall make the simple and very reasonable assumption that all four carbons are equally involved in the bonding to the metal; this implies that the three carbon–carbon bonds within the butadiene unit are all affected equally. The structural evidence[1–3,18–21] shows that a symmetrical arrangement of $Fe(CO)_3$ with respect to the butadiene unit gives the most satisfactory bonding. The only plausible complication would be to allow for the possibility that the terminal carbons may be slightly more localized than the central carbons.

Using the simplest numerical choices which reflect the above conclusions, we obtain a successful model for the calculation of localization energies. The carbon–carbon resonance integrals of the hydrocarbon are modified as follows: for each of the three carbon–carbon bonds within the butadiene unit under discussion the resonance integral is reduced from β to 0.5β; for each carbon–carbon bond of the hydrocarbon involving only one carbon of the butadiene unit, to 0.75β;[23] and for each bond between carbons involved in different butadiene units (when the addition of two $Fe(CO)_3$ groups is under consideration), to 0.5β; all other resonance integrals, and all Coulomb integrals, α, are unchanged.

Styrene is a suitable example: the first of the two figures below gives the reduced resonance integrals, in units of β, appropriate to discussion of the possibility of an $Fe(CO)_3$ group adding to the butadiene unit 8,7,1,2; the second figure does likewise for the butadiene unit 3,4,5,6. (The numbering is as in Table I.) The possibility of a diderivative, involving both butadiene units, is discussed by reducing all eight resonance integrals to 0.5β.





Some limited variation of this model toward the unsuccessful extremes mentioned above is also compatible with the qualitative experimental data, though the quantitative predictions would be altered. In particular an increase in the localization of the terminal carbons is permissible. The fact that the most successful models are those which accord most closely with physical and theoretical expectation provides support for our approach.

The partial localization energy, the difference between the delocalization energy of the unperturbed hydrocarbon with all resonance integrals β and that of the hydrocarbon with the reduced resonance integrals, can be calculated by standard methods.[11] Since the calculations are laborious without a computer, it may be helpful to point out that a useful guide to the results can be readily obtained from the bond orders, if these are available,[24] by first-order perturbation theory.[11,24] While these approximate results differ slightly from the calculated values, particularly for molecules with other than six-membered rings, the trends are similar. To minimize the uncertainty in our treatment, this approximation has been rejected.

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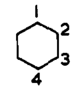
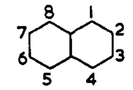
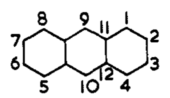
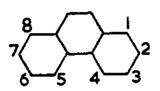
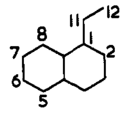
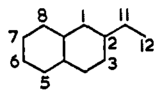
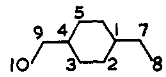
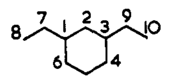
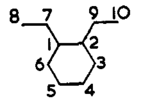
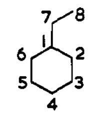
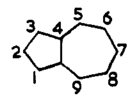
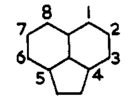
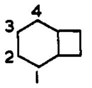
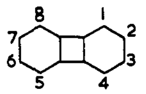
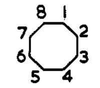
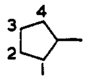
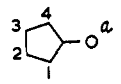
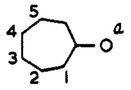
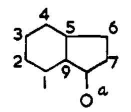
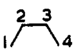
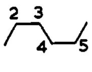
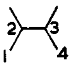
[22] M. Cais and N. Maoz, *J. Organometal. Chem.* (Amsterdam), **5**, 370 (1966).

[23] A good case could be made for reducing these resonance integrals to 0.707β, the geometric mean of β and 0.5β. The distinction would be important in a more localized model, but here it makes little difference to the qualitative conclusions (for mono derivatives the only change is that styrene and benzocyclobutadiene are predicted to be slightly less rather than slightly more reactive than anthracene, issues on which the experimental evidence is not decisive). Discussion of such a detailed point as this is best left until quantitative information becomes available.

[24] A. Streitwieser, Jr., C. A. Coulson, and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Pergamon Press, New York, N. Y., 1965.

Table I. Partial Localization Energies for Some Butadiene Units

Unsaturated hydrocarbon	Butadiene unit(s)	L_B or L_{BB} ($L_{B'}$)
	1,2,3,4	2.659
	1,2,3,4 {1,2,3,4 5,6,7,8}	2.598 5.201 (2.603)
	1,2,3,4 9,11,12,10 {1,2,3,4 5,6,7,8}	2.586 2.804 5.172 (2.586)
	1,2,3,4 {1,2,3,4 5,6,7,8}	2.604 5.203 (2.599)
	12,11,1,2 5,6,7,8 {5,6,7,8 12,11,1,2}	2.536 2.600 5.137 (2.601)
	12,11,2,1 12,11,2,3 5,6,7,8 {5,6,7,8 12,11,2,1} {5,6,7,8 12,11,2,3}	2.529 2.552 2.594 5.127 (2.598) 5.139 (2.587)
	8,7,1,2 {8,7,1,2 10,9,4,5} {8,7,1,2 10,9,4,3}	2.557 5.103 (2.546) 5.120 (2.563)
	8,7,1,2 8,7,1,6 {8,7,1,6 10,9,3,4} {8,7,1,2 10,9,3,4}	2.537 2.555 5.100 (2.545) 5.103 (2.566)
	8,7,1,6 3,4,5,6 {8,7,1,6 10,9,2,3}	2.544 2.601 5.098 (2.554)
	8,7,1,2 3,4,5,6 {8,7,1,2 3,4,5,6}	2.563 2.631 5.212 (2.649)
	5,6,7,8 1,2,3,4 {1,2,3,4 6,7,8,9} {1,2,3,4 5,6,7,8}	2.552 2.684 5.236 (2.684) 5.242 (2.690)
	1,2,3,4 {1,2,3,4 5,6,7,8}	2.715 5.436 (2.721)
	1,2,3,4	2.549
	1,2,3,4 {1,2,3,4 5,6,7,8}	2.597 5.186 (2.589)
	1,2,3,4 {1,2,3,4 5,6,7,8}	2.314 4.828 (2.514)
	1,2,3,4	2.518
	1,2,3,4	2.387
	1,2,3,4 2,3,4,5	2.552 2.573
	1,2,3,4 9,5,6,7 {1,2,3,4 9,5,6,7}	2.550 2.763 5.364 (2.814)
	1,2,3,4	2.236
	1,2,3,4 2,3,4,5	2.379 2.594
	1,2,3,4	2.258

[a] For the oxygen atom Coulomb integral, α_O, a value of $\alpha + \beta$ was used; β was retained for the carbon–oxygen resonance integral.[11]

Table I reports the results of this approach for several hydrocarbons and a few ketones. The unsaturated carbon skeleton is given in the first column; the next column defines the butadiene units for which results are given, with mono- and diderivatives considered. The third column gives the partial localization energies in terms of the localization indexes L_B, L_{BB}, and $L_{B'}$; following Streitwieser[11] these are defined as the dimensionless numbers obtained on dividing the loss of delocalization energy by β. L_B refers to a monoderivative, and L_{BB} to a diderivative. $L_{B'}$, given in parentheses below L_{BB}, refers to the increase in the partial localization energy consequent upon changing from the more stable (lower L_B) of the two possible intermediate monoderivatives to the diderivative.

All plausible butadiene units for these molecules have been considered, but only the more important results are presented here; other positions usually have $L_B > 2.7$ and $L_{BB} > 5.4$. Strictly, in estimating the rate of reaction of a hydrocarbon all the butadiene units should be allowed for; in practice, because the rate depends exponentially on the activation energy it is usually sufficient to consider only the most reactive positions.[10c] A statistical factor is necessary to allow for the possibility of equivalent butadiene units; this factor is usually 1 or 2 in the cases discussed here, though its value is not always obvious by inspection (for example, for benzene it will be between 1 and 6, probably about 2).

Styrene is again a convenient example; if $Fe(CO)_3$ is attached to the butadiene unit 8,7,1,2 the partial localization energy will be 2.563β, but for the unit 3,4,5,6 it will be 2.631β. If both butadiene units are involved the total partial localization energy will be

5.212β (note that in general the value of L_{BB} is not equal to the sum of the two relevant values of L_B). As the diderivative will presumably be formed by the addition of an $Fe(CO)_3$ group to the stabler of the two monoderivatives, a guide to the ease of preparation of the diderivative can be obtained from the difference between the value of L_{BB} and the value of L_B for the monoderivative more easily formed; in this case $L_B = 5.212 - 2.563 = 2.649$.

This approach to diderivatives is similar to that used for diadducts in the Diels–Alder reaction,[10a] where, however, there is no doubt about the appropriate description of the hydrocarbon after the first stage of the reaction. For simplicity we have assumed that the butadiene unit in a fully formed monoderivative is not much more localized than in the preceding transition state; we have then used our model of this transition state as a starting point for discussing the addition of a second $Fe(CO)_3$ group. The results are most sensitive to this assumption when the second butadiene unit is close to the first.

If the localization energy approach is successful there will be a critical value of L_B below which monoderivatives can be obtained, but above which reaction is too slow to be useful. There will similarly be a critical value of $L_{B'}$ for the addition of a second $Fe(CO)_3$ group. This value should be about the same as the critical value of L_B; it may not be exactly the same because of the effects of the first $Fe(CO)_3$ group. For example, the addition of one electron-donating[1] $Fe(CO)_3$ group to a hydrocarbon may render further addition of electron-donating groups more difficult, other things being equal; the critical value of $L_{B'}$ would then be slightly lower than that of L_B. When the two $Fe(CO)_3$ groups are some way apart such effects will probably be small (and variable from one compound to another); but when they are close enough for direct steric and electronic interactions between the two groups the situation is uncertain. We shall find below that if L_B is less than about 2.59, the formation of monoderivatives is observed; the experimental evidence does not determine the critical value of $L_{B'}$ so exactly.

The following discussion is based on results for reactions between hydrocarbons and iron carbonyls carried out at elevated temperatures; this is the standard preparative procedure.[1] Accurate rates of reaction and, with one exception, results for competitive reactions between different hydrocarbons are lacking. As with Diels–Alder addition[10a,b] we must be content with qualitative correlations based on yields and refluxing times. The evidence is insufficient to justify detailed consideration of the reaction conditions, such as the temperature or the particular iron carbonyl from which the $Fe(CO)_3$ moiety is derived. We can only say that predictions refer to typical experimental conditions. (Most of the key reactions to be discussed, including those with polyacenes, their vinyl derivatives, acenaphthylene, and tropone, were performed by refluxing with triiron dodecacarbonyl, $Fe_3(CO)_{12}$. With iron pentacarbonyl, $Fe(CO)_5$, longer reaction times and higher temperatures are needed.[1] Diiron enneacarbonyl, $Fe_2(CO)_9$, often gives iron tetracarbonyl ($Fe(CO)_4$) derivatives.[1]) While the relative rates of reaction of different hydrocarbons should be qualitatively similar for more forceful preparative methods, the range of hydrocarbons from which derivatives could be obtained would be extended (that is, the critical value of L_B would be higher).

Bearing all these remarks in mind, we shall now consider the hydrocarbons in their order in Table I.

Results and Discussion

$Fe(CO)_3$ Derivatives. Benzene has not been reported to give a derivative.[4] (Also no derivatives were obtained from various methyl-substituted benzenes.[5] A comment for all these hydrocarbons is that electron-withdrawing substituents are more likely to lead to $Fe(CO)_3$ derivatives because of the electron-donating tendencies of $Fe(CO)_3$, and because the delocalized system of the substituted hydrocarbon is more easily disturbed. An obvious example is that the cyclopentadienylrhodium group, which is not as renowned as $Fe(CO)_3$ for bonding to butadiene units, succeeds in bonding to a butadiene unit of a benzene nucleus in hexakis(trifluoromethylbenzene)cyclopentadienylrhodium.[25])

Despite early reports to the contrary naphthalene does not give a derivative, even after 64 hr of refluxing at 130°.[4] However, after 48 hr at 90°, anthracene does give a 3% yield of monoderivative (the crude yield was "much higher"),[4] despite an earlier negative result;[5] no diderivative is obtained, and $Fe(CO)_3$ is bonded to the terminal ring, in contrast to Diels–Alder addition but as indicated by the values of L_B (or by intuitive reasoning[4]). These results show that the critical value of L_B is less than 2.598 and slightly greater than 2.586 for which value a monoderivative can be obtained with difficulty. The value of $L_{B'}$ for anthracene is also 2.586; however, the diderivative should be formed more slowly than the monoderivative because of the statistical factor of 2 in favor of the first stage of the reaction (besides other possible complications already mentioned). With the low yield of monoderivative, isolation of the diderivative would not be expected even if both stages of the reaction proceeded at the same rate.

No information is available for phenanthrene, which is conveniently considered here. It should react less readily even than naphthalene; this suggests that the forecast of derivatives for aromatic hydrocarbons more extended then naphthalene[4] should be accepted with caution. Predictions for the terminal rings of many extended polyacenes can be obtained by noting whether the last three rings of the hydrocarbon are arranged linearly like anthracene (in which case reaction should be possible), or angularly like phenanthrene (if so, reaction is unlikely). For example, the results for the terminal butadiene units of tetracene are $L_B = L_{B'} = 2.582$.

1-Vinylnaphthalene gives, after 16 hr of refluxing at 90°, a 31% yield of a monoderivative, but no diderivative; the vinyl group is directly involved in the bonding with $Fe(CO)_3$.[4] This all agrees with the calculated values of L_B and $L_{B'}$. There is no information for 2-vinylnaphthalene which should also form a monoderivative; the orientation of $Fe(CO)_3$ relative to the hydrocarbon can be predicted.

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[25] M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 365 (1963).

p-Divinylbenzene gives a 29% yield of a diderivative after 18 hr of refluxing in benzene; after refluxing for 6 hr in benzene, a 2:1 *m*-:*p*-divinylbenzene mixture gives only a diderivative of *m*-divinylbenzene, in 20% yield. The vinyl groups are probably involved in the bonding; no monoderivatives are obtained.[5] All this is in agreement with the values of L_{B} and $L_{\mathrm{B'}}$: *m*-divinylbenzene should react more readily (a result which is not a numerical artifact, but is insensitive to plausible variations in the model of the transition state); both isomers should react more easily than anthracene; diderivatives should be readily formed; the vinyl groups should be involved. Too much significance should not be attached to the values of $L_{\mathrm{B'}}$ and L_{BB}. For neither hydrocarbon can we hope to predict which of the two most likely structures for the diderivative will be preferred. The two $Fe(CO)_3$ groups are too close together, both being bonded to the same benzene ring, and possibly to adjacent butadiene units. The predictions on this point implied by the values of L_{BB} can be easily reversed by small changes in the model of the transition state, and reversed again by considering direct steric interactions between the two $Fe(CO)_3$ groups. For *m*-divinylbenzene the situation is further complicated by the possibility of intramolecular rearrangement during the reaction; the preferred diderivative may not have a butadiene unit in common with the preferred intermediate monoderivative. There is no report on *o*-divinylbenzene which is predicted to behave similarly; in competition it should be more reactive than *p*- but less reactive than *m*-divinylbenzene.

Styrene is predicted to form a monoderivative, and to do so less readily than 1-vinylnaphthalene and *p*-divinylbenzene, but slightly more readily than anthracene.[23] (In making these comparisons allowance must be made for the statistical factor of 2 in favor of *p*-divinylbenzene and anthracene. Later remarks indicate that this is probably equivalent to a change of between 0.01 and 0.02 in the value of L_{B}; there is then little to choose between styrene and anthracene.) Experimentally, it has been reported that styrene does not react with $Fe_3(CO)_{12}$;[5] this is compatible with the above forecasts, since it was the same paper which reported the preparation of the divinylbenzene derivatives, but the failure of attempts to obtain an anthracene derivative. It has also been found that styrene does not react with $Fe(CO)_5$, probably because of polymerization of styrene.[26] It is relevant to note that indene, with the same unsaturated skeleton as styrene, reacts readily to give diindenyldiiron tetracarbonyl;[6] presumably this reaction proceeds *via* an indene–iron carbonyl complex, and a plausible mechanism involves the (indene)$Fe(CO)_3$ derivative which is the analog of the expected styrene derivative.[27] A more vigorous pursuit of (styrene)$Fe(CO)_3$ might well be successful.

Azulene should give a monoderivative, with $Fe(CO)_3$ bonded to the seven-membered ring; in fact, a diiron pentacarbonyl derivative, of uncertain structure, is obtained.[7] This sort of result is outside the scope of the present discussion; we should only be surprised if azulene gave no iron carbonyl derivative at all. No forecast of the structure is possible.

The high values of L_{B} and $L_{\mathrm{B'}}$ for acenaphthylene rule out any $Fe(CO)_3$ derivatives of the sort we are considering; the most favorable positions are those given in Table I. In the light of these arguments the acenaphthylene derivative once thought to be of this type, with two $Fe(CO)_3$ groups,[6] would be expected to have a different structure. Originally a prediction, this suggestion has recently proved correct; the compound has been identified as a diiron pentacarbonyl derivative[28] (which we again cannot discuss).

A monoderivative of unstable[11] benzocyclobutadiene has been prepared indirectly from dibromobenzocyclobutene; $Fe(CO)_3$ is bonded to the cyclobutadiene ring rather than to a butadiene unit of the benzenoid ring; further reaction does not occur.[26,29] These results do not contradict the indication from the value of L_{B} that a normal $Fe(CO)_3$ derivative should be obtainable more easily than for anthracene.[23] Not only is the preparation indirect, but also there is no reason why $Fe(CO)_3$ should not prefer the cyclobutadiene ring. As for further reaction, the steric and electronic effects of the first $Fe(CO)_3$ group will be too severe to allow worthwhile predictions about reaction at the adjacent butadiene unit.

For biphenylene the situation is clearer; formation of normal $Fe(CO)_3$ derivatives would not be expected according to the value of L_{B}. This prediction has recently been confirmed; biphenylene does not react with $Fe(CO)_5$.[26] (It is obvious in terms of localization energies that $Fe(CO)_3$ is less likely to be bonded to a cyclobutadiene ring in biphenylene than in benzocyclobutadiene or cyclobutadiene.)

Cyclooctatetraene gives both mono- and diderivatives, with the mono- in higher yield;[8] this is as we might have expected from the values of L_{B} and $L_{\mathrm{B'}}$. However, these values were calculated from a planar model; since cyclooctatetraene assumes various nonplanar structures on its own and as a ligand,[1,21] this correlation is not as reliable as the rest of our discussion.

Substituted fulvenes and cyclopentadienones give monoderivatives,[1] as we would expect. Unsubstituted cyclopentadienone is unstable, but its $Fe(CO)_3$ derivative has been prepared indirectly from acetylene.[1]

The monoderivative of tropone is readily prepared from tropone;[30] the values of L_{B} correctly forecast the favored butadiene unit.[1,19,20,31]

Indenone is another unstable ketone,[11] but the monoderivatives of two substituted indenones have been obtained indirectly;[9] the evidence implies that $Fe(CO)_3$ bonds to the ketonic rather than to the benzenoid ring, in sharp contradiction with the values of L_{B}. There are some possible explanations for this, our only failure. Firstly, the indirect method of preparation may lead irrevocably to this product. Secondly, this may be a case where the lowest vacant orbital becomes decisive. For indenone this orbital is nonbonding and so will be particularly accessible and important; the orbital is localized $^7/_{19}$ on the ketonic butadiene unit and $^4/_{19}$ on the benzenoid butadiene unit (9,5,6,7 and 1,2,3,4, respectively, with the numbering of Table I),

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(26) G. F. Emerson, private communication.

(27) *Cf.* ref 1, p 24.

(28) R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).

(29) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

(30) E. Weiss, W. Hübel, and R. Merényi, *Ber.*, **95**, 1155 (1962).

(31) E. H. Braye and W. Hübel, *J. Organometal. Chem.* (Amsterdam), **3**, 25 (1965).

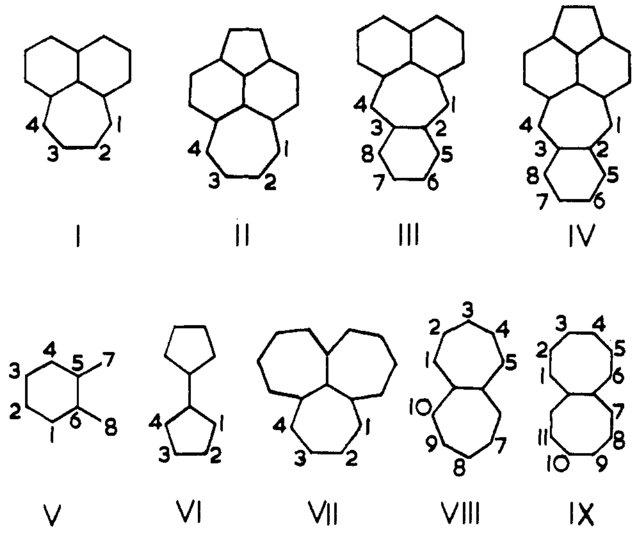

Figure 1. The unsaturated skeletons of some hydrocarbons which should form $Fe(CO)_3$ derivatives.

which may lead $Fe(CO)_3$ to prefer the former.[32] Thirdly, polarization of the ketonic carbonyl group could lead to bonding like that in the (cyclopentadienyl)$Fe(CO)_3$ cation;[1] it is relevant to note that $Fe(CO)_3$ derivatives of the fulvene skeleton show a strong tendency to give cyclopentadienyl derivatives.[1] This would be outside the scope of our discussion.

(butadiene)$Fe(CO)_3$ is of course well known.[1] The hexatriene skeleton should form a monoderivative; various examples have been reported, such as (cycloheptatriene)$Fe(CO)_3$.[1] The terminal butadiene units are favored, as indicated by the values of L_B. It has been suggested[33] that $Fe(CO)_3$ moves less rapidly around the skeleton of tropone and hexatriene than around cyclooctatetraene because in the former cases the butadiene units encountered are not all equivalent; the values of L_B for the various butadiene units of tropone and hexatriene lend weight to this hypothesis.

A monoderivative of 2,2′-bis(π-allylene) would be expected; in fact, a diiron hexacarbonyl derivative with an iron–iron bond has been obtained indirectly.[34] Again, this is not of present interest.

All in all, a sufficient amount of experimental data can be qualitatively correlated to justify the use of this approach. It may be objected that the correlation is based on very small differences in the values of L_B. Though the differences seem smaller than is usual in localization energy indexes, this is only because we have used a partially localized model; the trends will still be significant. And since we would expect to use a normal value for β (of, say, -40 kcal) in quantitative correlations, rather than the smaller values often necessary in completely localized models, the actual energy differences we are working with will not be much smaller than usual. Furthermore the quantitative predictions seem reasonable; at 90° with $\beta = -40$ kcal and allowing for the statistical factor, 1-vinylnaphthalene should react faster than anthracene (for which the value of L_B is 0.05 higher) by a factor of $e^{(-0.05\beta/RT)}/2$, *i.e.*, about 8. As an order of magnitude estimate this is by no means inconsistent with the experimental results. Since quantitative predictions are sensitive to the exact description of the transition state, serious discussion must be left until accurate observations become available.

The main limitation of this approach has already become clear; only one type of iron carbonyl derivative, albeit the most common, is considered. This limitation qualifies any prediction. As further examples we note cyclopentadienyl and cycloheptatrienyl, both of which have low values of L_B; in fact, in both cases the product contains an iron atom attached to a positively charged five-membered carbon unit of the hydrocarbon.[1]

We have also ignored factors connected with the configuration of the butadiene unit. A planar *cis* configuration is required, but for some of the butadiene units discussed above, including butadiene itself, other configurations are more stable. For the divinylbenzenes there are obvious complications of this type. The situation is similar to that discussed for Diels–Alder addition.[10b] Even for polyacenes, where this ambiguity does not appear, other steric effects may accelerate or retard the reaction.[35] Another limitation concerns substituted hydrocarbons; the important effects of substituents[1,22] cannot be easily allowed for. Also no predictions can be offered as to whether $Fe(CO)_3$ groups in diderivatives will be bonded to the same or opposite sides of the hydrocarbon; either situation may occur.[36]

There is no reason in principle why localization energies should not be useful for other types of iron carbonyl derivatives, but there is not yet enough information to allow such discussion. For example, $Fe(CO)_4$ derivatives, in which the iron atom interacts with a "double bond" of the hydrocarbon, could obviously be considered in terms of the bond localization energies used to discuss the addition of OsO_4[10c] (though a partially localized model may be needed for the reasons already given). Using $Fe_2(CO)_9$, $Fe(CO)_4$ derivatives of styrene, acenaphthylene, butadiene, and substituted fulvenes have been prepared.[1,29,37] One can at once predict that $Fe(CO)_4$ derivatives of the divinylbenzenes should be obtainable, but until a few negative results have been reported the scope of this reaction will remain unclear. Ultimately it may be possible to predict not only which hydrocarbons will form a particular type of derivative, but also which type of derivative will be obtained from a given hydrocarbon and a given iron carbonyl. For the moment we can only discuss $Fe(CO)_3$ derivatives; some predictions follow.

Predictions for $Fe(CO)_3$ Derivatives. The following predictions are, with one or two exceptions, insensitive to the model of the transition state. Some structures and numbering are given in Figure 1.

9-Vinylanthracene will provide a good test of the present approach; it should react like anthracene rather than like 1-vinylnaphthalene (L_B = 2.589 and

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[32] *Cf.* D. A. Brown and G. N. Schrauzer, *Z. Physik. Chem.*, **36**, 1 (1963).

[33] H. W. Whitlock, Jr., and Y. N. Chuah, *J. Am. Chem. Soc.*, **87**, 3605 (1965).

[34] A. Nakamura and N. Hagihara, *J. Organometal. Chem.* (Amsterdam), **3**, 480 (1965).

[35] Reference 11, p 344.

[36] C. E. Keller, G. F. Emerson, and R. Pettit, *J Am. Chem. Soc.*, **87**, 1388 (1965).

[37] E. K. von Gustorf, M. C. Henry, and C. di Pietro, *Z. Naturforsch.*, **21b**, 42 (1966).

$L_{B'}$ = 2.590 for the butadiene units in the terminal rings; L_B = 2.656 for the butadiene unit incorporating the vinyl group).

$Fe(CO)_3$ should add to the butadiene unit 1,2,3,4 in the seven-membered ring of cycloheptanaphthylene (I) (L_B = 2.515) and similarly for cycloheptacenaphthylene (II) (L_B = 2.528); Diels–Alder addition only succeeds with the former.[11] It should also be possible to add $Fe(CO)_3$ to the unit 5,6,7,8 of both pleiadene (III) (L_B = 2.568) and acepleiadylene (IV) (L_B = 2.576), though with difficulty; $Fe(CO)_3$ should not add to the seven-membered ring (for example, to the unit 1,2,3,4 of either hydrocarbon), in contrast to Diels–Alder addition.[38] As an example of a large conjugated system which should not accept $Fe(CO)_3$ we note fluoranthene (L_B = 2.605 for the most isolated butadiene unit).

o-Xylylene (V) is an unstable hydrocarbon isolated in dimeric forms,[39] but it may be possible to obtain $Fe(CO)_3$ derivatives (L_B = 2.397 for the unit 7,5,6,8; $L_{B'}$ = 2.580 for the unit 1,2,3,4); the monoderivative should be formed readily, but analogy with benzocyclobutadiene suggests that the diderivative will not be easily obtainable.

Heptafulvene is another unstable molecule[11] which it may be possible to isolate as an $Fe(CO)_3$ derivative. With the same numbering as for tropone in Table I, the values of L_B for the units 1,2,3,4 and 2,3,4,5 are, respectively, 2.523 and 2.544.

Neutral fulvalene (VI) polymerizes but the dianion is stable;[11] both should take up two $Fe(CO)_3$ groups to the butadiene units of the type 1,2,3,4 if the values of L_B are interpreted directly. However, we are only justified in discussing neutral molecules since the critical value of L_B will be quite different if a charged hydrocarbon is involved; presumably electron-donating $Fe(CO)_3$ will bond most easily to cationic hydrocarbons. For neutral fulvalene L_B = 2.419 and $L_{B'}$ = 2.465. Pleiaheptalene (VII) has not yet been reported; the dication should be stable.[11] Three butadiene units of type 1,2,3,4 are accessible; for the neutral molecule L_B = 2.362, $L_{B'}$ = 2.464, and $L_{B''}$ = 2.493, where $L_{B''}$ has an obvious meaning.

Heptalene (VIII) polymerizes readily;[40] $Fe(CO)_3$ derivatives should be obtainable. The prediction is for a diderivative, not involving the two carbons joining the rings. Two types of isomers satisfying this requirement are possible (we shall ignore distinctions caused by bonding to different sides of the unsaturated system): *trans*, with the butadiene units 2,3,4,5 and 7,8,9,10 (L_B = 2.478, $L_{B'}$ = 2.488), and *cis*, with the units 1,2,3,4 and 7,8,9,10 (L_B = 2.478, $L_{B'}$ = 2.501). The *trans* is favored, with a value of L_{BB} 0.013 lower than for the *cis*. There are two isomers of each type; interconversion between the two *trans* isomers must proceed *via* a *cis* isomer and *vice versa*. Octalene (IX) has not yet been reported; it will probably be planar and stable.[11] It may well be prepared as a diderivative. There are four possible types of isomers, excluding those involving the two carbons which link the rings. Examples of each type, in order of increasing value of L_{BB}, involve the following butadiene units: 1,2,3,4 and 7,8,9,10 (L_B = 2.472, $L_{B'}$ = 2.464); 3,4,5,6 and 7,8,9,10 (L_B = 2.472, $L_{B'}$ = 2.468); 2,3,4,5 and 7,8,9,10 (L_B = 2.472, $L_{B'}$ = 2.497); and 2,3,4,5 and 8,9,10,11 (L_B = 2.509, $L_{B'}$ = 2.501). The third of these isomers will be the intermediate for the interconversion of the first two (which are analogous to the *trans* and *cis* isomers of heptalene). The above predictions of the preferred isomers cannot be altered as easily as can those for the diderivatives of the divinylbenzenes, so they should be more reliable. The temperature dependence of the nmr spectra of these derivatives will be of special interest.

These suggestions for unstable hydrocarbons depend on the fact that unstable molecules can be trapped as stable organometallic compounds, as was successfully[29] forecast[41] for cyclobutadiene. For octalene a more direct organometallic synthesis may be possible; 2,2′-bis(π-allylene)diiron hexacarbonyl, mentioned above, seems a suitable intermediate for the preparation of $Fe(CO)_3$ derivatives of octalene. These stable $Fe(CO)_3$ derivatives of hydrocarbons which are unstable, or otherwise hard to synthesize, would not merely be curiosities; they would be convenient sources of the hydrocarbons since the free ligand can be obtained fairly readily.[42] A notable example is the recent liberation of cyclobutadiene from its $Fe(CO)_3$ derivative.[42]

$Cr(CO)_3$ Derivatives. Some interesting trends have been observed for $Cr(CO)_3$ derivatives of polycyclic hydrocarbons. The limited qualitative evidence[6,43–47] allows us to distinguish two groups of hydrocarbons: first, benzene, naphthalene, phenanthrene, and chrysene; and second, anthracene, tetracene, pyrene, and acenaphthylene. Members of the first group on the whole give stabler derivatives more easily. Crystals of (benzene)$Cr(CO)_3$ are stable in air for a long time;[43] (phenanthrene)$Cr(CO)_3$ and (chrysene)$Cr(CO)_3$ are of comparable stability to (naphthalene)$Cr(CO)_3$.[6] Crystals of (pyrene)$Cr(CO)_3$ decompose completely on standing in air for several months, unlike (naphthalene)$Cr(CO)_3$ and (phenanthrene)$Cr(CO)_3$.[6] (anthracene)$Cr(CO)_3$ seems to be less stable than (phenanthrene)$Cr(CO)_3$. When thoroughly dry, crystals of the anthracene derivative in air have been described as tolerably stable,[47] and as stable for some time.[45] The descriptive evidence suggests that in organic solvents (anthracene)$Cr(CO)_3$ decomposes more readily than (benzene)$Cr(CO)_3$ or (phenanthrene)$Cr(CO)_3$;[43,45,47] indeed, in some solvents the anthracene derivative decomposes at once.[45] (In solutions exposed to air even (benzene)$Cr(CO)_3$ decomposes after several hours.[43])

These trends are confirmed by the variations in the ease of formation of these derivatives from chromium hexacarbonyl ($Cr(CO)_6$) and the appropriate

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[38] M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3051 (1965); we use their nomenclature, not that of ref 11.

[39] L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

[40] H. J. Dauben, Jr., and D. J. Bertelli, *ibid.*, **83**, 4659 (1961).

[41] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

[42] L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).

[43] E. O. Fischer and K. Öfele, *Ber.*, **90**, 2532 (1957).

[44] B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959), and references therein.

[45] B. R. Willeford, Jr., and E. O. Fischer, *J. Organometal. Chem.* (Amsterdam), **4**, 109 (1965), and references therein.

[46] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Ber.*, **91**, 2763 (1958).

[47] E. O. Fischer, N. Kriebitzsch, and R. D. Fischer, *ibid.*, **92**, 3214 (1959).

hydrocarbon. (phenanthrene)$Cr(CO)_3$ was obtained in 27% yield after refluxing for 2.25 hr.[6] Under similar conditions it was found that derivatives of pyrene and acenaphthylene were obtained with more difficulty (*i.e.*, lower yields in longer times);[6] that (anthracene)$Cr(CO)_3$ was obtained only in trace amounts and could not be isolated[6] (though isolation has since been achieved[45]); and that chrysene gave a derivative, but tetracene did not.[6] Using a similar reaction other workers have obtained good yields of the benzene and naphthalene derivatives.[44,46] Despite the uncertain evidence, it is clear that either decreasing the number of condensed rings in a linear acene from four (tetracene) to one (benzene), or rearranging the rings in an angular manner (from tetracene to chrysene, or from anthracene to phenanthrene), encourages the formation of $Cr(CO)_3$ derivatives.[6]

In using a localization energy approach for $Cr(CO)_3$ derivatives we shall consider the final compound rather than the transition state. It is to be expected that the larger the necessary localization energy, the less stable the derivative. As for the ease of formation, it was noted earlier that equilibria rather than activation energies may be decisive; this is supported by the instability of the products, and by the fact that reaction is facilitated if the carbon monoxide displaced from $Cr(CO)_6$ can escape[44] (the formation of $Fe(CO)_3$ derivatives from $Fe_3(CO)_{12}$ is simpler in this respect since $Fe_2(CO)_9$ is an obvious product). Whatever the details, it is reasonable to assume that large localization energies will imply preparative difficulties.

It is well established that $Cr(CO)_3$ bonds to a benzenoid ring rather than to a butadiene unit in these derivatives.[43-49] Proceeding as before, we shall assume that it is the interaction of the whole benzene ring with $Cr(CO)_3$ which determines the properties of a derivative, rather than, say, a particular double bond; this is supported both by the structural evidence[48,49] and by the rate of formation of derivatives of various substituted benzenes.[44] In calculating localization energies all six carbons in the benzenoid ring should therefore be equally localized (the ambiguity introduced for butadiene units by the possible distinction between terminal and central carbons is absent here). The only remaining question concerns the appropriate degree of localization, which may alter the predictions for the same reasons as before. If the degree of localization corresponds to that used above for $Fe(CO)_3$ derivatives, then there is no correlation between the partial localization energies and experiment; however, as the degree of localization is increased a definite correlation rapidly emerges. This correlation is particularly clear if the benzenoid ring is completely localized. Although later results may change the situation, at the moment there is no need to introduce the complication of a partially localized model. For $Cr(CO)_3$ derivatives the localization energy can conveniently be taken as the loss of resonance energy when all six carbons of the appropriate benzenoid ring are completely removed from the unsaturated system of the hydrocarbon.

The localization energies given below refer in each case to the benzenoid ring predicted to be the most favorable; this can be unambiguously described as a terminal ring for all the hydrocarbons except pyrene, where it is the ring whose removal leaves a "residual molecule"[10a,b] of *m*-divinylbenzene rather than of decapentaene. That $Cr(CO)_3$ should always be found bonded to a terminal rather than a central ring of polyacenes is intuitively obvious[47] and has been confirmed for phenanthrene[49] and anthracene.[45] In order of increasing localization energies, the results are: benzene (8.00β), phenanthrene (9.02β), chrysene (9.06β), naphthalene (9.21β), anthracene (9.36β), tetracene (9.40β), acenaphthylene (9.63β), and pyrene (9.66β).

These results reproduce the trends observed for linear and angular polyacenes. It is of particular interest to compare the $Fe(CO)_3$ and $Cr(CO)_3$ derivatives of the polyacenes. Localization energies correctly predict that both $Fe(CO)_3$ and $Cr(CO)_3$ will be bonded to a terminal ring; that $Fe(CO)_3$ derivatives will be more likely, but $Cr(CO)_3$ derivatives less likely, along the linear acene series from benzene to tetracene; and that $Cr(CO)_3$ derivatives will be more likely with angular than with linear polyacenes. To complete the comparison it only remains to confirm that $Fe(CO)_3$ derivatives are less likely with angular than with linear polyacenes. The correlation of these diverse trends is a significant success for Hückel localization energy approximations. It should be emphasized that this achievement is not an artifact of our use of a partially localized model for $Fe(CO)_3$ derivatives but a completely localized model for $Cr(CO)_3$ derivatives. Firstly, the qualitative predictions obtained for $Fe(CO)_3$ derivatives of these polyacenes if the butadiene unit is completely localized are the same as in our partially localized model. Secondly, it is just about possible to choose a degree of localization which will simultaneously correlate all the results for $Fe(CO)_3$ derivatives and those for $Cr(CO)_3$ derivatives. Thirdly, it is quite likely that a more localized model is appropriate for $Cr(CO)_3$ derivatives, both because the discussion is in terms of the final compound rather than the transition state and because $Cr(CO)_3$ is electron withdrawing rather than electron donating.

The physical reasons for these results are worth elaboration. Taking completely localized models, formation of an $Fe(CO)_3$ derivative is less likely from phenanthrene than from anthracene because the residual molecule is naphthalene in both cases, and phenanthrene has the more resonance energy to lose. This factor also operates in favor of anthracene for $Cr(CO)_3$ derivatives but is outweighed by the fact that the residual molecule from phenanthrene is now styrene, while from anthracene it is the less favored *o*-xylylene. It is because of these competing effects that the correlation for $Cr(CO)_3$ derivatives only emerges clearly after a certain degree of localization.

The correlation is not entirely satisfactory for pyrene and acenaphthylene; their behavior relative to anthracene and tetracene would not have been predicted from the localization energies.

We have not considered diderivatives, which are quite possible for phenanthrene as far as localization energies are concerned. Experiment indicates that the electron-withdrawing effect of one $Cr(CO)_3$ group is sufficient to prevent further reaction. Nor shall we offer many predictions; as for $Fe(CO)_3$ derivatives,

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forecasts for the terminal rings of many extended polyacenes can be obtained by comparing the last three rings of the hydrocarbon to anthracene or phenanthrene. Thus triphenylene, a very angular hydrocarbon, should be more favorable than phenanthrene toward $Cr(CO)_3$ derivatives, but the reverse for $Fe(CO)_3$ derivatives. As another example, both 1,2-benzopyrene and 4,5-benzopyrene should give $Cr(CO)_3$ derivatives more satisfactorily than anthracene; the existence of a $Cr(CO)_3$ derivative of benzopyrene (which isomer was unspecified) has been reported, but no details are available.[6] For a final contrast with $Fe(CO)_3$ derivatives we note that biphenylene should give a $Cr(CO)_3$ derivative without difficulty; the localization energy of a benzenoid ring is only 8.51β. For hydrocarbons where the benzenoid ring is only linked to the remaining unsaturated system at one carbon the localization energy is usually less than 8.5β; $Cr(CO)_3$ derivatives of many such hydrocarbons are known, for example, biphenyl,[47] 1,4-biphenylbutadiene,[5] and stilbene.[50] Insofar as a completely localized model proves acceptable, further predictions for $Cr(CO)_3$ derivatives can be easily deduced from the available molecular orbital data.[24]

The present methods could obviously be applied to other metal carbonyl derivatives, such as those with cobalt tricarbonyl bonded to an allyl group. There is, however, little information on allyl units in aromatic hydrocarbons, though the recently reported[51] π-benzylcyclopentadienylmolybdenum dicarbonyl has the metal interacting with the exocyclic allyl unit of the benzyl moiety, as is forecast by a partial localization energy approach. For completeness we should mention that the ability of hydrocarbons to form complexes with silver cations has been discussed in terms of bond orders[52] and delocalization from the hydrocarbon to the cation;[53] both approaches are intimately related to localization energies.[10d,11,12]

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Iron(II) Chelates of N,N′-Disubstituted Aminotroponeimines

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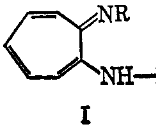
Abstract: Fe(II) chelates of representative aminotroponeimines have been synthesized and characterized. These paramagnetic chelates show large contact shifts in the nmr, and both solution and solid-state magnetic susceptibility studies show the presence of four unpaired electrons. Marked differences in reactivity of the chelates toward various complexing agents were found, and these are attributed to steric effects arising from shielding of the tetrahedral iron atom by substituents attached to nitrogen.

The synthesis and properties of N,N′-disubstituted aminotroponeimines (I) and of their nickel chelates have been reported.[1] Aminotroponeimines (ATI) are regarded as nonclassical aromatic systems on the basis of chemical and physical studies. Their paramagnetic nickel chelates are of special interest since large proton shifts have been observed in nuclear magnetic resonance studies. Through these studies information has been obtained on the manner in which an unpaired electron is delocalized into π systems.[2]



I

This paper describes the preparation and properties of paramagnetic iron(II) chelates of I, where R is methyl, ethyl, *t*-butyl, phenyl, and *p*-tolyl. Methods analogous to those used for the preparation of nickel(II) chelates gave iron(III) chelates in certain instances but failed to give the corresponding iron(II) derivatives. However, two syntheses were uncovered that with one exception yielded the desired iron(II) products. These procedures are (1) reaction of aminotroponeimines with iron pentacarbonyl in an open vessel and (2) reaction of N-lithioaminotroponeimines with anhydrous ferrous chloride. Of the two methods, the latter is preferred.

These procedures appear general, except for the

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