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Molecular Orbital Theory of Organometallic Compounds, Part 4. Substitution Reactions of Tricarbonyl-benzenechromium

by

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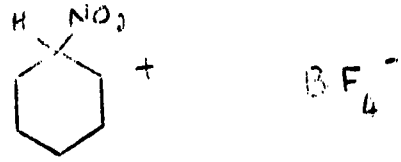
This paper constitutes part of a series based on the application of simple empirical molecular orbital theory to organometallic compounds. In Part 3 (1), it was shown that such theory provided a satisfactory explanation of the charge transfer observed in substituted tricarbonylbenzenechromiums, $XC_6H_5Cr(CO)_3$; in the present paper this theory is extended to a discussion of the substitution reactions of these systems. In particular, we shall calculate the contribution of the π-electron energy, ΔE_π^*, to the activation energy for nucleophilic, radical, and electrophilic substitution of the complex and compare these values with those for the corresponding substitution reactions of benzene. The calculations are made for a wide range of parameters in order to test the reliability of the conclusions made on such a theoretical model.

It is first necessary to consider the most probable transition state for this reaction; it is assumed that the transition state for substitution in the complex is the same as for benzene and is of the Wheland type; that is, that the carbon atom undergoing substitution is effectively removed from the conjugated system which now embraces only five of the six ring carbon atoms in the case of benzene and five carbon atoms and the $Cr(CO)_3$ fragment in the case of the complex (Fig. 1). There has been much discussion as to the nature of this transition state but recent views (2) give support to the above type; in particular, it has been shown by Olah (3) that stable σ-complexes of the type



can be isolated. The parallelism between, for example, the logarithm of the rate constant for protodeuteration of methylbenzenes and the log. of their relative equilibrium constants with hydrogen fluoride shows that a close similarity between the transition state for substitution and the above type of complex is most probable. It seems reasonable then to assume that a change in π-electron energy ΔE_{π}^{+} between the ground state and the above structure will produce a parallel effect, $k^{1} \Delta E_{\pi}^{+}$, in the actual transition state. Since it is comparative values which we require this is sufficient. In addition, of course, final comparison between the calculated energies and observed substitution reactions must involve the usual assumption of the neglect of entropy differences. In view of the similar nature of the reactions this assumption is probably more valid here than in most cases.

Figure 1.

Calculation

In the case of benzene, removal of one carbon atom (C_1) from conjugation changes the electron configuration in the ground state from $a_1^2 e_1^4$ to $(1a_1)^2 \ (1b_2)^2 \ (2a_1)^n$ for the transition state where a_1 and b_2 denote π-orbitals which are symmetric and antisymmetric respectively with respect to the symmetry plane

through atoms C_1 and C_4 and n is 0, 1 or 2 for electrophilic, radical, and nucleophilic substitution respectively. It is a simple matter to show by Huckel theory that the difference in π-electron energies of the two states is:

$$\Delta E_{\pi}^{+}(\text{benzene}) = -((2-n)H_{cc} + 2{\cdot}536\beta_{cc})$$

where H_{cc} is the usual Huckel Coulomb term of the carbon $2p_{\pi}$ orbital and β_{cc} the resonance integral between two such orbitals. It is customary to regard the $2a_1$ orbital as non-bonding since it lies at exactly the same energy as the free $2p_{\pi}$ orbital of carbon but in this case the matter is more complicated.

For both the complex and its transition state, it is necessary to consider the interaction of the above π-orbitals with the various metal orbitals; these may be classified by symmetry as shown in Table 1. It should be noted that the two antisymmetric orbitals $1b_2$ and $2b_2$ in the transition state are identical with one component of each of the doubly-degenerate e_1 and e_2 orbitals of benzene.

Table 1.

The magnitudes of the interactions are estimated by means of the group overlap integrals which were calculated in exactly the same way as discussed in Part 3 of this series and using standard tables (4). However, in this paper we solve the usual secular determinant:-

$$\left| H_{ij} - S_{ij}E \right| = 0$$

where H_{ij} is the resonance integral between orbitals ψ_i and ψ_j and S_{ij} is the corresponding overlap integral, i and j run over all the ring π-orbitals and the chromium 3d, 4s and 4p orbitals, by assuming that $H_{ij} = kS_{ij}$ and allowing k to vary over the wide range of k = 1·0 to 7·0 (2·0). In this manner, a considerable variation in the strength of the interaction between the π-orbitals and the metal orbitals is permitted. The above relationship is explicit in the semi-empirical treatment and has been used by many authors (5); it is gratifying to note that the recent detailed calculations, using the S.C.F. method of ferrocene by Dahl and Ballhausen (6) give support to the relation. In the previous treatment of ferrocene by Dunitz and Orgel (7) good agreement with observed bond energies was obtaind using a k value of about five but these authors neglected the interaction of the 4p orbitals. The authors (8) showed subsequently that such interaction was considerable and the above detailed calculations support this. It appears, therefore, that reasonable values of k lie below 5·0. The Coulomb terms of the chromium orbitals were again (as in Part 3) taken from the spectroscopic values of Berry (9) and also (as in Part 3) the Coulomb term of the π-orbitals by identifying the first ionization potential of benzene with $H(e_1e_1)$; the positions of the other π-orbitals both in the ground state and the transition state were then determined relative to this term in terms of β_{cc} which was allowed the values 1·0, 2·0 and 3·0 to cover a wide variation in β values. The orbital energies of both the

complex and the transition state were then evaluated by solving the above determinant for this range of parameters using an IBM 1620 computer. For the complex this involved the solution of two (2x2) and one (4x4) determinant but with the lower symmetry of the transition state, solution of two (2x2) determinants for the b_2 group and one (9x9) determinant for the a_1 group are required. In this way all possible interactions, including the weakest, were included. Table 2 gives the values of the group overlap integrals employed in these calculations.

Table 2.

Neglecting the σ-bonds of the $Cr(CO)_3$ fragment, the ground state configuration of the complex is:

$$(1a_1)^2 (1e_1)^4 (2a_1)^2 (1e_2)^4$$

and of the transition state is:

$$(1a_1)^2 (1b_{2y})^2 (2a_1)^2 (3a_1)^2 (1b_{2xy})^2 (4a_1)^n$$

where n is defined as above. It is then a simple matter to evaluate the total π-electron energies of the complex and the transition state for different types of substitution and hence the π-electron activation energies for the complex, ΔE_π^+.

The total activation energy for such substitution reactions will be given by the expression:

$$\Delta E^+ = \Delta E_\pi^+ + (2-n)\,\Delta E_H^+ + \Delta E_B^+$$

where ΔE_π^+ is the difference in π-electron energies of

ground state and transition state,

ΔE_H^+ is the difference in hybridization energy between the carbon atom in the sp^3 and $sp^2\pi$ valence states,

ΔE_B^+ is the difference in bond energies between the ground state and transition state.

The second term is independent of the attacking reagent and it is generally assumed that the third term is also fairly constant (although detailed kinetic investigations by Dewar and co-workers (10) of aromatic nitration reactions suggest that this may not always be a correct assumption). However, in comparing the activation energy for substitution of the complex and of benzene by a given reagent it is reasonable to assume that the second and third terms will be identical and hence any differences will be due solely to changes in the π-electron activation energy, ΔE_π^+. In this way values of the relative activation energy, R.A.E., where:

$$\text{R.A.E.} = \Delta E_\pi^+ \text{ (benzene)} - \Delta E_\pi^+ \text{ (complex)}$$

were calculated for nucleophilic, radical, and electrophilic substitution. In order to calculate this expression for the last two types of substitution it is necessary to assign a value to H_{cc}, the Huckel Coulomb integral of the carbon $2p_\pi$ orbital. This was done from our previous identification of the highest filled orbital coulomb term, $H(e_1e_1)$, with the ionization potential of benzene. The different values of H_{cc} then appropriate to the given β_{cc} value are given in Table 3, together with the final results for the relative activation energies (R.A.E.).

Table 3.

Discussion

It follows from equation 1 that our conclusions for nucleophilic substitution are independent of the Coulomb term, H_{cc}, and depend only upon the value of the resonance integral β_{cc}. For all values of β_{cc} greater than 2·0 e.v. and k values less than 5·0, it follows from Table 3 that the relative activation energy is positive. In other words, the activation energy for nucleophilic substitution of the complex is less than that of benzene and so such substitution should occur more easily for the former compound. As stated above, k values of greater than 5·0 lead to too large bond energies for these systems. A value of β_{cc} lying between 2·0 and 3·0 e.v. is in good agreement with the values obtained, viz. 2·48 and 3·41 e.v., from a correlation of the ionization potentials and molecular orbital energies of a wide range of conjugated systems (11).

In the case of radical and electrophilic substitution, explicit account must be taken of the Coulomb term H_{cc}. In the transition state of the complex, the difference between the three types of substitution lies in the filling up of the $4a_1$ orbital. Inspection of the eigenvectors of this orbital shows that for the above range of parameters k and β_{cc}, it is primarily a non-bonding 3d orbital; the difference then between nucleophilic, radical, and electrophilic substitution for a given k and β_{cc} will depend upon the relative magnitudes of H_{3d3d} and H_{cc}. Thus for

$$|H_{cc}| > |H_{3d3d}|$$

$$\text{R.A.E. (Elec.)} > \text{R.A.E. (nucl.)}$$

and vice-versa as shown in the Table for the cases $\beta = 2{\cdot}0$ and $\beta = 3{\cdot}0$. There is then some ambiguity in any deductions drawn concerning electrophilic and radical substitution in these complexes arising from the uncertainties in the value of H_{cc}. The above correlation, for example, of ionization potentials gives the values $H_{cc} = 6{\cdot}24$ and $7{\cdot}07$ e.v. which unfortunately are values which are respectively less than and greater than H_{3d3d}. However, for the reasonable range $\beta_{cc} \gtrsim 2{\cdot}5$ e.v., it follows from Table 3 that the relative activation energies are only slightly positive or in some cases negative. Our conclusions regarding electrophilic substitution are more tentative than those for nucleophilic substitution but it is apparent that the rates of electrophilic substitution should not differ greatly for the complex as compared to benzene. The difference for nucleophilic will be much greater. This is particularly evident if we confine our attention to the case of $\beta_{cc} = 3{\cdot}0$ e.v.. It is interesting to note that the above theoretical treatment shows that simple predictions (12) based on the assumption that the $Cr(CO)_3$ group is electron-attracting and hence equivalent to, for example, a nitro group, require some modification. Indeed, as pointed out generally (13), any treatment of kinetic effects requires consideration of the effect of a group upon both ground state and transition state before the hazarding of any predictions.

Comparison with Experiment

No detailed kinetic or even competition experiments have

yet been performed on this complex so there is no quantitative data available for comparison with the above theory. However, simultaneously with the discovery of these compounds, Whiting and co-workers (12) reported that nucleophilic substitution was greatly enhanced relative to the benzene analogues. Thus tricarbonylchlorobenzenechromium was converted into the anisole complex in good yield at 65° which is in marked contrast to the unreactivity of chlorobenzene itself. The results regarding electrophilic substitution are less clear since the above authors reported a marked lack of reactivity in, for example, Friedel Crafts acylation experiments. However, two other groups (14) have reported up to 80% yields of, for example, tricarbonylacetaphenonechromium from tricarbonylbenzenechromium under the quite mild conditions of refluxing in carbon disulphide. Recent studies (15) of acylation of tricarbonyltoluenechromium do suggest, however, that the complex reacts more slowly than the parent arene.

It is evident that detailed kinetic studies of both electrophilic and nucleophilic substitution are required for comparison with the theoretical predictions of this paper.

I should like to thank Miss Leahy, Physics Department, University College, Dublin, for her kind help with the computing, and the U.S. Office of Naval Research for a grant.

Table 1

Symmetry Classification of Orbital Interactions in Complex and Transition State

π-Orbitals of Benzene	Orbital Energy (β)	Metal Orbitals	π-Orbitals in T.S.	Orbital Energy (β)	Ligand (CO) Orbitals
a_1	-2·00	$4s 4p_z 3d_{z^2}$	$1a_1$	-1·732	$a_1(CO)$
e_{1x}	-1·00	$3d_{xz}, 4p_x$	$2a_1$	0·000	$e_{1x}(CO)$
$e_{2x^2-y^2}$	-1·00	$3d_{x^2-y^2}$	$3a_1$	+1·732	-
e_{1y}	-1·00	$3d_{yz}, 4p_y$	$1b_{2y}$	-1·00	$e_{1y}(CO)$
e_{2xy}	+1·00	$3d_{xy}$	$2b_{2xy}$	+1·00	-

Table 2

Group Overlap Integrals for Complex and Transition State

Totally Symmetric Groups

ψ	$S(\psi,4s)$	$S(\psi,3d_{z^2})$	$S(\psi,4p_z)$	$S(\psi,3d_{xz})$	$S(\psi,4p_x)$	$S(\psi,3d_{x^2-y^2})$
			Complex			
a_1	0·207	0·072	0·022	-	-	-
			Transition State			
$1a_1$	0·1821	0·0633	0·0196	0·1233	0·1110	0·0203
$2a_1$	0·0488	0·0170	0·0053	0·1805	0·1626	0·1102
$3a_1$	0·0131	0·0045	0·0014	0·0331	0·0298	0·0753

Doubly-degenerate and Antisymmetric Groups

	$S(\psi,3d_{yz})$	$S(\psi 4p_y)$	$S(\psi,3d_{xy})$
			Complex
e_1	0·2708	0·2439	-
e_2	-	-	0·1654
			Transition State
$1b_{2y}$	0·2708	0·2439	-
$2b_{2xy}$	-	-	0·1654

Table 3

Relative Activation Energies (R.A.E.)

β_{cc}	k	R.A.E. (elec.) (e.v.)	R.A.E. (rad.) (e.v.)	R.A.E. (nucl.) (e.v.)
H_{cc} = 8·24				
1·0	1·0	+1·9006	+0·4370	-1·0266
	3·0	+1·3960	+0·0049	-1·3862
	5·0	+0·7570	-0·5477	-1·8524
	7·0	-0·0160	-1·2401	-2·4632
H_{cc} = 7·24				
2·0	1·0	+1·0256	+0·5491	+0·0726
	3·0	+2·2886	+1·18162	+1·3438
	5·0	+0·7442	+0·2798	-0·1846
	7·0	+0·1894	-0·2638	-0·7170
H_{cc} = 6·24				
3·0	1·0	+0·0624	+0·5856	+1·1088
	3·0	+0·1616	+0·6867	+1·2118
	5·0	-0·0048	+0·5240	+1·0528
	7·0	-0·3744	+0·1597	+0·6938

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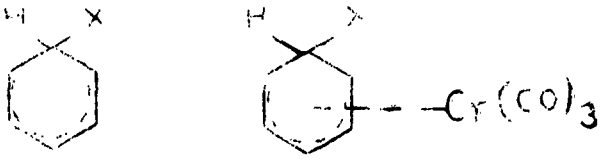

FIG. I

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