

841. *Molecular-orbital Theory of Organometallic Compounds. Part IV.¹
Substitution Reactions of Tricarbonylbenzenechromium.*

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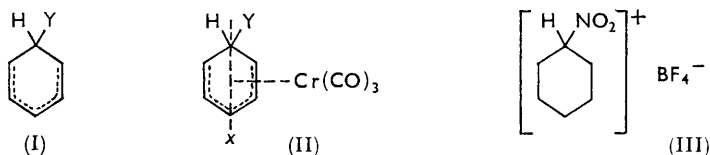
Substitution of tricarbonylbenzenechromium is discussed in terms of simple molecular-orbital theory applied to a Wheland-type transition state. It is shown that, for all reasonable values of the carbon-carbon resonance integral, nucleophilic substitution should occur more easily for the complex than for the parent arene. The conclusions for electrophilic and radical substitution are less definite, but the rate differences between reactions of the complex and of the arene should be much smaller in these cases. The theoretical predictions are compared with the available evidence.

THIS paper constitutes part of a series based on the application of simple empirical molecular-orbital theory to organometallic compounds. In Part III,¹ it was shown that such theory satisfactorily explains the charge transfer observed in substituted tricarbonylbenzenechromiums, $X \cdot C_6H_5Cr(CO)_3$; in the present paper it is extended to substitution of these compounds. In particular, we shall calculate the contribution of the π -electron

¹ Parts I and II, Brown, *J. Inorg. Nuclear Chem.*, 1959, **10**, 39, 49. Brown and Sloan, *J.*, 1962, 3849, is considered to be Part III.

energy, ΔE_{π}^{\dagger} , to the activation energy for nucleophilic, radical, and electrophilic substitution of the complex and compare these values with those for the corresponding substitution of benzene. The calculations are made for a wide range of parameters in order to test the reliability of the conclusions from the theoretical model.

We consider first 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, *i.e.*, that the carbon atom undergoing substitution is effectively removed from the conjugated system which then embraces only five of the six ring-carbon atoms in the case of benzene and five carbon atoms and the $\text{Cr}(\text{CO})_3$ fragment in the case of the complex (cf. I, II). There has been much discussion as to the nature of this transi-



tion state, but recent views² support the above type; in particular, Olah and Kuhn³ have shown that stable σ -complexes of type (III) can be isolated. The parallelism between, for example, the logarithm of the rate constant for protodeuteration of methylbenzenes and the logarithm of their relative equilibrium constants with hydrogen fluoride indicates close similarity between the transition state for substitution and the above type of complex. It seems reasonable then to assume that a change in π -electron energy ΔE_{π}^{\dagger} between the ground state and the above structure will produce a parallel effect, $k'\Delta E_{\pi}^{\dagger}$, in the actual transition state. Since we require only comparative values this suffices. Final comparison between the calculated energies and the observed reactions must, as usual, neglect entropy differences, which, in view of the similar nature of the reactions, is probably more valid here than in most cases.

CALCULATIONS

In the case of benzene, removal of one carbon atom (C-1) from conjugation changes the electron configuration in the ground state from $a_1^2 e^4$ 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,

TABLE I.

Form of the π -orbitals of transition state of benzene.						
Orbital	Energy (β)	C-2	C-3	C-4	C-5	C-6
$1a_1$	-1.7321	+0.2887	+0.5000	+0.5773	+0.5000	+0.2887
$2a_1$	0.0000	+0.5773	—	-0.5773	—	+0.5773
$3a_1$	+1.7321	-0.2887	+0.5000	-0.5773	+0.5000	-0.2887
$1b_2$	-1.0000	+0.5000	+0.5000	—	-0.5000	-0.5000
$2b_2$	+1.0000	+0.5000	-0.5000	—	+0.5000	-0.5000

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. The detailed form of these orbitals is given in Table I. It is a simple matter to show by Hückel theory that the difference in π -electron energies of the two states is:

$$\Delta E_{\pi}^{\dagger}(\text{Benzene}) = -[(2-n)H_{\text{CO}} + 2.536\beta_{\text{CO}}], \quad (1)$$

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

² Streitwieser, "Molecular Orbital Theory for Organic Chemists," J. Wiley, New York, 1961, p. 313; de la Mare and Ridd, "Aromatic Substitution," Butterworths Scientific Publns., London, 1959.

³ Olah and Kuhn, *J. Amer. Chem. Soc.*, 1958, **80**, 6542.

For both the complex and its transition state, it is necessary to consider interaction of the above π -orbitals with the various metal orbitals; these may be classified by symmetry and both

TABLE 2.

Symmetry classification of orbital interactions in complex and transition state.

π -Orbitals of benzene	Orbital energy (β)	Metal orbitals	π -Orbitals in transition state	Orbital energy (β)	Ligand (CO) orbitals
a_1	-2.00	$4s, 4p_z, 3d_{z^2}$	$1a_1$	-1.732	$a_1(\text{CO})$
e_{1z}	-1.00	$3d_{xz}, 4p_x$	$2a_1$	0.000	$e_{1z}(\text{CO})$
$e_{2x^2-y^2}$	+1.00	$3d_{x^2-y^2}$	$3a_1$	+1.732	—
e_{1y}	-1.00	$3d_{yz}, 4p_y$	$1b_{2y}$	-1.00	$e_{1y}(\text{CO})$
e_{2xy}	+1.00	$3d_{xy}$	$2b_{2xy}$	+1.00	—

the complex and transition state are given in Table 2. It should be noted that the two anti-symmetric 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.

Application of the variational theorem to this problem leads to the usual secular determinant:

$$|H_{ij} - S_{ij}E| = 0,$$

where H_{ij} is the resonance integral between orbitals ψ_i and ψ_j , and S_{ij} is the corresponding overlap integral, H_{ii} is the Coulomb term of the orbital ψ_i with i and j running over all the ring orbitals and the chromium $3d, 4s$ and $4p$ orbitals. As in Part III,¹ the Coulomb terms of the chromium orbitals were taken directly from Berry's spectroscopic values⁴ and the Coulomb terms of the π -orbitals were obtained by identifying the first ionisation potential of benzene with $H(e_1e_1)$:

$$H(e_1e_1) = H_{CC} + \beta_{CC} = 9.24 \text{ ev.}$$

The positions of the other π -orbitals in the ground and the transition state were determined relative to this term in terms of β_{CC} which was allowed the values 1.0, 2.0, and 3.0 ev to cover a wide range of β values. For example, for benzene:

$$H(a_1a_1) = 9.24 + \beta_{CC}.$$

The resonance integral H_{ij} was evaluated from the assumption that $H_{ij} = kS_{ij}$, and k was allowed a wide variation in the range 1.0—7.0 ev (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 relation is explicit in the semi-empirical treatment and has been used by many authors;⁵ it is gratifying that recent detailed calculations,⁶ by the self-consistent-field method, of ferrocene support it. In the previous treatment of ferrocene by Dunitz and Orgel⁷ good agreement with observed bond energies was obtained by using a $k = \sim 5$ ev, but these authors neglected interaction of the $4p$ orbitals. The present author⁸ showed later that such interaction was considerable and the detailed calculations⁶ support this; it appears, therefore, that reasonable values of k lie below 5 ev. The group overlap integrals were calculated as in Part III, from tables.⁹ For example, the formula for the overlap integral between a totally symmetric ring π -orbital and the $4p_z$ -orbital of chromium is:

$$S(\psi, 4p_z) = \sum_{i=1}^m C_i [(S_i(2p_\sigma 4p_\sigma) \cos^2 \theta_i - S_i(2p_\pi 4p_\pi) \sin^2 \theta_i)],$$

where C_i is the coefficient of the i 'th carbon atom in the given molecular orbital, and θ_i is the angle between the z axis and the M- C_i vector; the integer m takes the value 5 for the transition state and 6 for the ground state.

For the complex this involved the solution of two (2×2) and one (4×4) determinant, but

⁴ Berry, *J. Chem. Phys.*, 1961, **35**, 29.

⁵ Mulliken, *J. Chim. phys.*, 1949, **46**, 500; Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173; Brown, *J.*, 1961, 691.

⁶ Dahl and Ballhausen, *Kgl. danske Videnskab. Selskab. Mat.-fys. Skrifter*, 1961, **33**, 1.

⁷ Dunitz and Orgel, *J. Chem. Phys.*, 1955, **23**, 984.

⁸ Brown, *J. Chem. Phys.*, 1958, **29**, 1086.

⁹ Jaffe, *J. Chem. Phys.*, 1953, **21**, 258; Leiffer, Cotton, and Leto, *ibid.*, 1958, **28**, 364; Brown, *ibid.*, 1958, **29**, 1086.

with the lower symmetry of the transition state solution of two (2×2) determinants for the b_2 group and one (9×9) determinant for the a_1 group is required. In this way all possible interactions, including the weakest, were included. Table 3 gives the values of the group overlap integrals employed in these calculations.

TABLE 3.

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.							
ψ	$S(\psi, 3d_{yz})$	$S(\psi, 4p_y)$	$S(\psi, 3d_{xy})$	ψ	$S(\psi, 3d_{yz})$	$S(\psi, 4p_y)$	$S(\psi, 3d_{xy})$
Complex				Transition state			
e_1	0.2708	0.2439	—	$1b_{2y}$	0.2708	0.2439	—
e_2	—	—	0.1654	$2b_{2xy}$	—	—	0.1654

Neglecting the σ -bonds of the $\text{Cr}(\text{CO})_3$ fragment, we obtain the ground-state configuration of the complex as

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

and of the transition state as

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

where n is defined as above. The symbol $1a_1$, for example, denotes an orbital which is largely a mixture of the ring π -orbital of this type ($1a_1$) and metal orbitals (hybrids if one so wishes to consider them) directed towards the ring. It is simple 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^\ddagger .

The total activation energy for such substitutions is given by

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

where ΔE_π^\ddagger is the difference in π -electron energies of ground state and transition state, ΔE_H^\ddagger is the difference in hybridisation energy between the carbon atom in the sp^3 and $sp^2\pi$ valency states, ΔE_B^\ddagger is the difference in bond energies between the ground state and the 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 his co-workers¹⁰ of aromatic nitration suggests that this may not always be correct). 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, so that any differences will be due to changes in the π -electron activation energy, ΔE_π^\ddagger . In this way values of the relative activation energy, $[\Delta E_\pi^\ddagger(\text{Benzene}) - \Delta E_\pi^\ddagger(\text{Complex})]$ were calculated for nucleophilic, radical, and electrophilic substitution. For radical and electrophilic substitution it is necessary to assign a value to H_{CC} , the Hückel 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 ionisation potential of benzene. The different values of H_{CC} then appropriate to the given β_{CC} value are given in Table 4, with the final results for the relative activation energies.

¹⁰ Dewar, Mole, and Warford, *J.*, 1956, 3581.

TABLE 4.

Relative activation energies (r.a.e.)							
k (ev)	R.a.e. (elec.) (ev)	R.a.e. (rad.) (ev)	R.a.e. (nucl.) (ev)	k (ev)	R.a.e. (elec.) (ev)	R.a.e. (rad.) (ev)	R.a.e. (nucl.) (ev)
	$H_{CC} = 8.24$ ev; $\beta_{CC} = 1.0$ ev				$H_{CC} = 7.24$ ev; $\beta_{CC} = 2.0$ ev		
1.0	+1.9006	+0.4370	-1.0266	1.0	+1.0256	+0.5491	+0.0726
3.0	+1.3960	+0.0049	-1.3862	3.0	+2.2886	+1.1816	+1.4338
5.0	+0.7570	-0.5477	-1.8524	5.0	+0.7442	+0.2798	-0.1846
7.0	-0.0160	-1.2401	-2.4632	7.0	+0.1894	-0.2638	-0.7170
	$H_{CC} = 6.24$ ev; $\beta_{CC} = 3.0$ ev.						
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				

DISCUSSION

It follows from equation (1) that our conclusions for nucleophilic substitution are independent of the Coulomb term, H_{CC} , and depend only on the value of the resonance integral β_{CC} . For all values of β_{CC} greater than 2.0 ev and k values less than 5.0, it follows from Table 4 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 greater than 5.0 lead to too large bond energies for these systems). A value of β_{CC} between 2.0 and 3.0 ev agrees well with those obtained (2.48 and 3.41) from a correlation of the ionisation potentials and molecular-orbital energies of a wide range of conjugated systems.¹¹

For radical and electrophilic substitution, 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 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 on the relative magnitudes of H_{3d3d} and H_{CC} . Thus for

$$|H_{CC}| > |H_{3d3d}|,$$

and *vice-versa* as shown in Table 4 for the cases $\beta = 2.0$ and 3.0 ev. There is then some ambiguity in deductions concerning electrophilic and radical substitution in these complexes, arising from the uncertainties in the value of H_{CC} . The above correlation, for example, of ionisation potentials gives the values $H_{CC} = 6.24$ and 7.07 ev, which unfortunately are values respectively less and greater than H_{3d3d} . However, for the reasonable range $\beta_{CC} \geq 2.5$ ev, $k > 3.0$ ev, it follows from Table 4 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 the rates of electrophilic substitution should not differ greatly for the complex and for benzene. The difference for nucleophilic substitution will be much greater. This is particularly evident if we confine our attention to the case $\beta_{CC} = 3.0$ ev. It is interesting that our theoretical treatment shows that simple predictions¹² based on the assumption that the $\text{Cr}(\text{CO})_3$ group is electron-attracting and hence equivalent to, for example, a nitro-group require modification. Indeed, as pointed out generally,¹³ any treatment of kinetic effects requires consideration of the effect of a group on both ground state and transition state before hazarding predictions.

¹¹ Ref. 1, various pp.

¹² Nicholls and Whiting, *J.*, 1959, 551.

¹³ Dewar, "Hyperconjugation," Ronald Press Co., New York, 1962.

Comparison with Experiment.—No detailed kinetic, or even competition, experiments have been performed on this complex, so there are no quantitative data for comparison. However, Nicholls and Whiting¹² 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°, in 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. However, two other groups¹⁴ reported yields up to 80% of, for example, tricarbonylacetophenonechromium from tricarbonylbenzenechromium under the mild conditions of refluxing carbon disulphide. Recent studies¹⁵ of acylation of tricarbonyltoluenecromium suggest, however, that the complex reacts more slowly than the parent arene.

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

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[Received, February 11th, 1963.]

¹⁴ Riemschneider, Becker, and Franz, *Monatsh.*, 1959, **90**, 571; Ercoli, Calderazzo, and Mantica, *Chimica e Industria*, 1959, **41**, 404.

¹⁵ Herberich and Fischer, *Chem. Ber.*, 1962, **95**, 2803.
