

### Preliminary communication

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## A METHOD FOR THE PREDICTION OF NUCLEOPHILIC ATTACKING SITES, AND ITS APPLICATION TO ATTACK BY METHOXIDE ON TRICARBONYLTROPYLIUMMETAL COMPLEXES

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### Summary

A method for computing the most favourable initial attacking site for a nucleophile on a transition metal complex is described, and its application to the nucleophilic attack of the methoxide anion on the cationic tricarbonyltropyliummetal complexes of chromium, molybdenum and tungsten reported. Initial attack at the metal atom in the molybdenum and tungsten complexes is successfully predicted, while the results of extended Hückel calculations on these systems correlate well with the final isolation of *exo*-ring addition products.

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The factors influencing the regioselectivity of nucleophilic additions to cyclic polyenetricarbonylmetal complexes are still not clear. Recent application [1] of the perturbation theory of reactivity [2–7] showed that the position of attack depends on both the nucleophilicity of the reagent and solvent polarity, with a possible changeover in the site of attack occurring on variation of these parameters. This method is preferable to the use of reactivity indices [8], since it explicitly considers both the nature of the nucleophile and solvent polarity. However the nucleophile (R) and substrate (S) are treated as point masses, and thus no consideration of the geometry of the (RS) system is made. In addition, the total orbital interaction energy  $(\Delta E_{RS})_{\text{orbital}}$  is assumed to be a summation of energies arising from pairwise interactions of each of the orbitals on R and S. Except in certain cases where the highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs) all belong to different irreducible representations of the point group of the molecule, this is incorrect.

In this note an alternative method for calculating  $(\Delta E_{RS})_{\text{orbital}}$  from a secular determinant based on MOs centred on the interacting R and S species is applied to the problem of regioselectivity. The determinant is constructed by

the extended Hückel (EH) method, using overlap and coulomb integrals between the MOs of R and S expressed as linear combinations of the basis functions of the orbitals. Solution of this determinant yields energy levels and orbitals for the combined RS system. By populating the lowest levels from the filled MOs, a value of  $(\Delta E_{RS})_{\text{orbital}}$  is calculated. The determinant may include as many MOs of the R and S systems as desired; for example, consideration can be restricted to a single HOMO—LUMO interaction, or, alternatively, steric effects due to repulsions between filled orbitals of R and S may be investigated by including such orbitals in the determinant. Moreover, the evaluation of overlap integrals between the MOs during solution of the determinant means that the relative orientations of the attacking species are explicitly included, and therefore, the preference for alternative paths of attack may be compared.

Since the MOs used in the determinant are computed using the isolated equilibrium geometries of the interacting molecules, the RS system considered corresponds to a very early point on the reaction coordinate. Therefore, this method is suitable for the prediction of initial attacking sites.

As an example, we consider the attack of the methoxide ion on the tricarbonyltropylium-chromium, -molybdenum and -tungsten cations.

The MOs of the complexes were calculated using the self-consistent charge and configuration (SCCC) EH method [9] and known geometries [10]. Orbital exponents were those of Fitzpatrick and Murphy [11]. Valence orbital ionisation potentials (VOIPs) [12,13] were used as approximations to the diagonal hamiltonian matrix elements. MOs were selected for inclusion in the “interaction determinant” by commencing at the HOMO and LUMO and working respectively downwards and upwards until a gap in energy between levels of 1 eV or greater was encountered. In this way, three HOMOs were included on each cation and two on the nucleophile, with five LUMOs on the chromium complex, eight on the molybdenum and ten on the tungsten.

Interaction energies calculated for geometries corresponding to ring, metal and carbonyl attack (see Fig. 1), at a fixed distance of 2 Å between the site of attack and the oxygen atom of methoxide are given in Table 1. In all cases, initial metal attack is predicted, in agreement with experiment for the molybdenum and tungsten compounds, but not for the chromium (see following paper); however, the differences between the energies of interaction for ring and carbonyl attack and metal attack widens from chromium to molybdenum and tungsten, due to inclusion of extra LUMOs for the latter compounds. These LUMOs are predominantly metal in character, and in the molybdenum and tungsten cases they are sufficiently low in energy to mix into the LUMO group, which in the chromium complex is produced by interaction of the type  $e''$  LUMO of the tropylium ring with the  $a_1$  and  $e' e''$  symmetry HOMOs and LUMOs of the  $M(\text{CO})_3$  fragment [14]. This increases the contribution of the metal in the LUMOs.

For attack on the chromium atom, orientation of the nucleophile on the  $C_3$  axis of the  $M(\text{CO})_3$  group is the most favourable, whereas “edge” attack produces a greater interaction for molybdenum and tungsten. Finally, no “crossovers” in attacking site with change in solvent polarity are predicted, in agreement with experimental observations. In fact, inclusion of the solvent term does not alter the prediction made using the orbital term at any polarity.

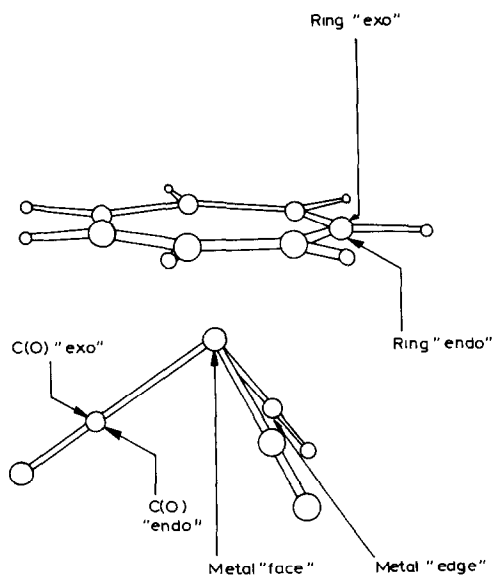


Fig. 1. Attacking geometries for tricarbonyltropyliummetal cations.

These predictions agree with those obtained using frontier charge density ( $\rho(\text{LUMO})$ ) values as a reactivity index [15]. The values for the  $\rho(\text{LUMO})$  summed over the LUMO groups are included in Table 1.

Total energies from EH calculations using the same attack geometries as the interaction calculations are also given. These show that in all cases the ring

TABLE 1

INTERACTION ENERGY, TOTAL ENERGIES AND  $\rho(\text{LUMO})$  VALUES FOR ATTACK OF METHOXIDE ON TRICARBONYLTROPYLIUMMETAL COMPLEXES

Complex	Site	$(\Delta E_{\text{RS}})_{\text{orbital}}$ (eV)	Total EH Energy (eV) <sup>a</sup>	$\Sigma\rho(\text{LUMO})$ (electrons)
$(\text{C}_7\text{H}_7)\text{Cr}(\text{CO})_3^+$	Ring <i>exo</i>	20.3	0.00	0.57
	Ring <i>endo</i>	20.4	+1.65	
	Metal <i>face</i>	22.4	+6.21	3.64
	Metal <i>edge</i>	21.2	+4.97	
	C(O) <i>exo</i>	20.4	+1.92	
$(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_3^+$	C(O) <i>endo</i>	21.7	+8.45	1.16
	Ring <i>exo</i>	19.9	0.00	
	Ring <i>endo</i>	20.0	+1.82	0.71
	Metal <i>face</i>	23.1	+5.95	
	Metal <i>edge</i>	25.8	+5.63	
$(\text{C}_7\text{H}_7)\text{W}(\text{CO})_3^+$	C(O) <i>exo</i>	19.8	+1.26	3.14
	C(O) <i>endo</i>	21.9	+8.56	
	Ring <i>exo</i>	21.3	0.00	0.76
	Ring <i>endo</i>	21.5	+1.66	
	Metal <i>face</i>	25.8	+5.69	5.90
	Metal <i>edge</i>	29.2	+5.08	
C(O) <i>exo</i>	21.3	+1.29		
	C(O) <i>endo</i>	23.7	+8.01	3.57

<sup>a</sup> Total energies are quoted relative to ring-*exo* attack for each complex.

*exo*-addition product is the most stable; *endo*-ring, carbonyl and metal attacks are destabilized by repulsions between the filled levels on the methoxide and the  $M(CO)_3$  fragment. This result agrees with that found by Astruc, Hoffmann and co-workers when studying attack by hydride on ( $\eta^5$ -cyclohexadienyl)-( $\eta^6$ -benzene)iron(II) [16], and correlates well with the isolation of *exo*-ring compounds as final products from reactions of alkoxy ions with the chromium, molybdenum and tungsten complexes (see following paper). Hence the EH method seems to be more applicable to the prediction of final products rather than initial sites, a role better filled by the interaction method introduced here.

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