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AN ATTEMPT AT INTERPRETING COMPETITIVE FRIEDEL-CRAFTS REACTIONS

ROLE OF SOLVATION ENERGY

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Abstract—Results of Olah *et al.* on benzylation of benzene and toluene are studied theoretically. The evolution of intermolecular k_T/k_B and intramolecular o/2p selectivities is interpreted with the aid of a model involving electron affinities of electrophilic entities. Our electrophilic affinities are calculated taking solvation into account, which reverses the order of affinities computed on the naked cations.

The Friedel-Crafts benzylation of benzene and toluene with benzyl and substituted benzyl chlorides has been investigated by Olah *et al.*[1] in the presence of various Lewis acid catalysts. In the present work we are concerned with results for relative reactivities of toluene and benzene in the $TiCl_4$ catalysed reactions.

$$C_6H_6 + C_6H_5{-}CH_3 + R{-}C_6H_4{-}CH_2Cl \xrightarrow{TiCl_4} C_6H_5{-}CH_2{-}C_6H_4{-}R + CH_3{-}C_6H_4{-}CH_2{-}C_6H_4{-}R$$

We attempted to interpret the evolution of toluene, -benzene intermolecular selectivities k_T/k_B and, for toluene alone, the evolution of intramolecular selectivities o/2p.

Partial rate factors for ortho and para toluene positions are given in Table 1. These partial rate factors show the reactivity of a toluene position relative to one of benzene. The k_T/k_B and o/2p ratios given by Olah *et al.* are also reported in this table.

These data show that the partial rate factors especially F_p increase from p-nitrobenzyl cation to p-methoxybenzyl cation. Likewise we notice an increase in k_T/k_B ratios and an increase in the attack on the para position.

Table 1. Partial rate factors and intermolecular and intramolecular selectivities for benzylation of toluene relative to benzene

R of $\lvert RC_6H_4CH_2\rvert^+$	F_o	F_p	(k_T/k_B)	(o/2p)
p–NO_2	4·5	5·1	2·5	0·87
H	7·6	20·9	6·3	0·37
p–F	11·2	26·4	8·7	0·43
p–CH_3	27·3	115·7	29·0	0·24
p–CH_3O	83·2	407·8	97·0	0·20

In these Friedel-Crafts reactions the electrophilic entity is a cation. The nitro group NO_2 is an electron withdrawing group and the methoxy group OCH_3 is an electron releasing group. Thus the methylene carbon positive charge will be larger with a nitro group than with a methoxy group. We note a greater reactivity difference between toluene and benzene with the p-methoxybenzyl cation which carries a smaller charge. The same is true for reactivity difference between the ortho and para positions. So reactivity order is not the same as charge order. It is well known that for certain reactions reactivity does not depend on charge. Klopman[2] has shown the competition between the charge-controlled and frontier-controlled reactions. Also, Bertran *et al.* have proposed[3] a theoretical model which takes this competition into account. We have successfully applied this model in previous work.[4-6] Therefore we used this model in studying the competitive benzylation reaction of toluene and benzene to interpret the evolution of k_T/k_B and o/2p ratios.

In this model, the electrophilic entity is represented by a non occupied orbital. The energy of this orbital is given by $E = \alpha + h\beta$ (Hückel method, α and β are negative parameters). According to an extension of Koopman's theorem[7] the energy level of this orbital reflects the electron affinity of the reagent. In this we determine the energy difference $E = E^{\pi}_{transition} - E^{\pi}_{substrate}$ where $E^{\pi}_{transition}$ is the energy of the transition state and $E^{\pi}_{substrate}$ is the π energy of the substrate. The closer the electron affinity of the reagent and the ionisation potential of the substrate the greater is the energy ΔE, this energy ΔE being a stabilisation energy.

We have plotted (Fig. 1) the relative stabilisation energies $(\delta E)_{o-b} = \Delta E_{toluene(ortho)} - \Delta E_{benzene}$ (curve 1) and $(\delta E)_{p-d} = \Delta E_{toluene(para)} - \Delta E_{benzene}$ (curve 2) for different values (from −1 to +1) of the h parameter which reflects electron affinity of the reagent. In all cases $\Delta E = E^{\pi}_{transition} - E^{\pi}_{substrate}$.

We notice from these curves that the values for $(\delta\Delta E)_{o-b}$ and $(\delta\Delta E)_{p-b}$, which reflect the intermolecular selectivity evolution k_T/k_B increase with h values. Furthermore $(\delta\Delta E)_{p-d}$ increases more rapidly than $(\delta\Delta E)_{o-b}$. Hence the values for $(\delta\Delta E)_{o-p} = \Delta E_{toluene(ortho)} - \Delta E_{toluene(para)}$, which reflect the evolution of the intramolecular selectivity o/2p, decrease with increasing h values. Accordingly these results agree with the evolution of k_T/k_B and o/2p ratios if the following order for h values is taken

$$h(p\text{–}OCH_3) > h(p\text{–}CH_3) > h(p\text{–}F) > h(H) > h(p\text{–}NO_2).$$

Thus the Bertran *et al.* reactivity model agrees with experimental results when the electron affinities decrease from p-nitrobensyl cation to p-methoxybenzyl cation.

We now calculate by Hückel and CNDO/2 methods charge densities and electron affinities of benzyl cations (Table 2). This will allow us to compare the sets of values given by Bertran *et al.* model with the sets of values given by Hückel and CNDO/2 calculations.

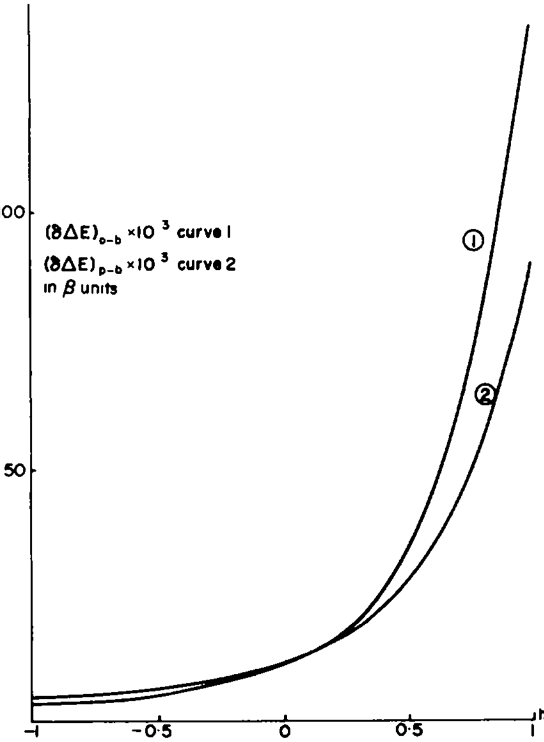

Fig 1. Plot of the stabilisation energy difference $(\delta E)_{o-b} = \Delta E_{toluene(ortho)} - \Delta E_{benzene}$ (curve 1) and $(\delta E)_{p-b} = \Delta E_{toluene(para)} - \Delta E_{benzene}$ (curve 2) against the electron affinity of the electrophilic reagent.

Table 2. Hückel and CNDO/2 methods

R of $\lvert R\text{–}C_6H_4CH_2\rvert$	Charges densities Hückel	CNDO/2	Electron affinities $h(E = \alpha + h\beta)$	CNDO/2 (eV)
$p\text{–}NO_2$	0·423	3·8759	+0·024	−7·3805
H	0·429	3·9076	0	−6·7256
p–F	0·423	3·9096	−0·023	−6·8428
$p\text{–}CH_3$	0·469	3·9276	−0·034	−6·5124
$p\text{–}OCH_3$	0·485	3·9289	−0·047	−6·5566

We notice that the positive charges decrease from p-nitrobenzyl cation to p-methoxybenzyl cation (Table 2). This is in agreement with electron accepting NO_2 and electron donating OCH_3 substituent effects; must be also noted, in accord with mass spectrometry results, that electron affinities decrease from p-nitrobenzyl cation to p-methoxybenzyl cation. The electron affinities order given by the Bertran *et al.* model (electron affinities of the cations in the reaction mixture) is therefore the reverse of our calculated order or of that determined by mass spectrometry (electron affinities in vapor phase 8). This reversal can be attributed to the solvation phenomenon. Each cation is solvated in the reaction medium. The more positive charge, the greater the solvation energy. This solvation energy is a cation stabilising energy. So a de-solvation energy must be available for the cation to react with aromatic hydrocarbons. This de-solvation energy is opposite in sign to the π delocalisation energy. The solvated cation electron affinities appear in Table 3. These affinities are given by:

$E^s_{af} = E_{af} + (E_r^s - E_c^s)$ (in β units)
E^s_{af}: solvated cation electron affinity
E_{af}: naked cation electron affinity
E_r^s: radical solvation energy
E_c^s: cation solvation energy

For solvation energy computation, we used Jano's expression[9]

$$E^s = -\left(1 - \frac{1}{\epsilon}\right)\left[\frac{1}{2}\sum_r Q_r^2\langle rr|rr\rangle + \sum_{\substack{r,s\\ r\neq s}} Q_r \cdot Q_s \langle rr|ss\rangle\right]$$

Q_i is the net charge of the i^{th} atom, $\langle rr|rr\rangle$ and $\langle rr|ss\rangle$ are mono and bicentric bielectronic repulsion integrals respectively (Pariser, Parr, Pople method). To conform with the Hückel method, calculations have been performed without iteration. In calculations, the $1/\epsilon$ term is not taken into account.

Table 3. Benzyl cations electron affinities (in β units).

R of $\lvert R\text{–}C_6H_4CH_2\rvert^+$	E_{af}	E_r^s	E_c^s	E^s_{af}
$p\text{–}NO_2$	+0·0242	1·4371	2·7687	−1·3074
H	0	0	1·0869	−1·0869
p–F	−0·0231	0·0052	1·0533	−1·0712
$p\text{–}CH_3$	−0·0342	0·0130	1·0338	−1·0550
$p\text{–}OCH_3$	−0·0466	0·0246	1·0285	−1·0506

It should be noted that the solvated cation electron affinities (Table 3) is reversed compared to the naked cation electron affinity order (Table 2). Thus, solvation reverses the cation electron affinity order, and in the transition state the smaller the induced cation π stabilisation energy the greater the cation positive charge. It follows that the k_T/k_B ratios are smaller and the o/2p ratios are greater. Let us point out that Olah *et al.* to justify the k_T/k_B and o/2p ratio evolution, suggest that along the reaction pathway the transition position is not fixed. To quote Olah *et al.*[1] "It can lie late on the reaction coordinate as reflected by high k_T/k_B rate ratios and low ortho/para ratios or it can be an early one reflected by low k_T/k_B rate ratios and high ortho/para isomer ratios". However it should be noted that for a given cation the k_T/k_B ratios decrease with increasing catalyst and solvant concentrations.[1] Therefore we prefer to interpret the k_T/k_B and o/2p ratio evolution by the solvation phenomenon. Moreover the solvation energy influence on chemical reactivity is well known.[10] For instance we remark the metal-halide complexe stability sequence reversal in water.[11]

In conclusion in the benzylation competitive reaction on benzene and toluene the intermolecular k_T/k_B and intramolecular o/2p selectivity evolution can be interpreted as a solvation effect. Cation solvation reverses the electron affinity order. For the transition state it follows that the stabilisation energy due to extension of the electron delocalisation is less important for the more positive cation. This leads to smaller k_T/k_B ratios and greater o/2p ratios.

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