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Theoretical Studies of the Effects of α-Substituents on the Resonance Demand of 4-Methoxybenzyl Carbocations[1]

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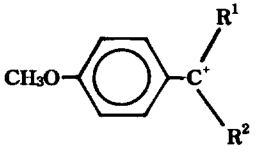
Abstract : Our AM1 results show that : (i) Electron-withdrawing polar effect of α-substituents leads to thermodynamic destabilization, $\delta \Delta H^0 > 0$, of benzylic carbocations. (ii) The increments of positive charge on C_α and on methoxy-O accompanying the carbocation formation are linearly correlated with the electron withdrawing polar effect, σ^* ; the positive charge on C_α is more strongly forced away onto the oxygen of the 4-methoxy group by a greater electron withdrawing power of the α-substituent.

Recently considerable attention of physical organic chemist has been directed to reactions involving carbocation intermediates bearing electron withdrawing substituents attached at the positive center. Richard et al.,[2] have shown that replacement of the α-methyl group with an α-trifluoromethyl in a 4-methoxy benzyl cation, Ic → If, has a large thermodynamic destabilizing polar effect, which is however offset to some extent by increased resonance electron donation from the 4-methoxybenzyl ring to the benzylic carbon. Thus the electron withdrawing polar effect of the α-substituent, R^1 and/or R^2, has been postulated to force the positive charge away from the benzylic carbon onto the oxygen of the 4-methoxy group.



I

	R^1 ;	R^2			
(a)	CH_3 ;	CH_3	(h)	H ;	H
(b)	H ;	t-butyl	(i)	H ;	$COOC_2H_5$
(c)	H ;	CH_3	(j)	H ;	C_6H_5
(d)	H ;	CH_2F	(k)	H ;	OCH_3
(e)	H ;	CHF_2	(l)	H ;	CN
(f)	H ;	CF_3	(m)	H ;	N_3
(g)	CF_3 ;	CF_3			

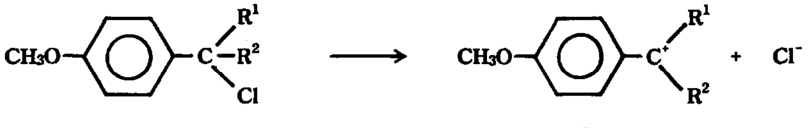
In this work, we show theoretically that there is a good linear correlation between the increment of positive charge on C_α and on the oxygen of the 4-methoxy group with the electron-withdrawing power of the α-substituents, R^1 and R^2, expressed by the Taft's polar substituent constants, σ^*.[3]

All calculations were carried out using the standard AM1 procedure.[4] Geometries of the reactants, R^1 and/or R^2 substituted benzyl chlorides, and their cations, Ia ~ Im, were fully optimized with no assumption. The results are summarized in Table 1. The enthalpies of reaction, ΔH^0, the increment of positive charge, $\Delta q = q_{(cation)} - q_{(reactant)}$, on C_α and on the oxygen atom of the

Table 1. The enthalpies of reaction, ΔH^0, increment of positive charges on $C_\alpha(\Delta q_{C\alpha}{}^+)$ and $O(\Delta q_O{}^+)$ in the process of $\underset{\text{React.}}{Y\text{-}C_6H_4CR^1R^2Cl} \longrightarrow \underset{\text{I}}{Y\text{-}C_6H_4C^+R^1R^2} + Cl^-$.

I	R^1, R^2	$\Sigma\sigma^*$		ΔH_f (kcal/mol)	ΔH^0 (kcal/mol)	$q(C_\alpha)$	$\Delta q(C_\alpha{}^+)$	q(O)	$\Delta q(O^+)$
a	CH_3 , CH_3	0.00	React.	-36.09	147.46	0.060	0.165	-0.210	0.061
			I	149.03		0.225		-0.149	
b	H , t-butyl	0.19	React.	-45.68	155.49	0.002	0.152	-0.210	0.067
			I	147.47		0.154		-0.143	
c	H , CH_3	0.49	React.	-35.10	156.64	-0.005	0.146	-0.209	0.067
			I	159.20		0.141		-0.142	
d	H , CH_2F	1.59	React.	-82.11	162.10	-0.048	0.108	-0.208	0.071
			I	117.65		0.060		-0.137	
e	H , CHF_2	2.54	React.	-131.61	168.12	-0.069	0.082	-0.207	0.079
			I	74.17		0.013		-0.128	
f	H , CF_3	3.10	React.	-182.41	172.63	-0.051	0.046	-0.206	0.085
			I	27.88		-0.005		-0.121	
g	CF_3 , CF_3	5.22	React.	-320.65	174.37	-0.034	-0.035	-0.202	0.093
			I	-108.62		-0.069		-0.109	
h	H , H	0.98	React.	-31.16	166.68	-0.067	0.129	-0.209	0.075
			I	173.18		0.062		-0.134	
i	H , C(=O)OEt	2.61	React.	-114.82	165.24	-0.005	0.073	-0.208	0.079
			I	88.08		0.068		-0.129	
j	H , C_6H_5	1.09	React.	0.15	150.36	0.035	0.152	-0.209	0.054
			I	188.17		0.187		-0.155	
k	H , OCH_3	2.30	React.	-67.82	147.45	0.126	0.114	-0.209	0.054
			I	-117.29		0.240		-0.155	
l	H , CN	3.79	React.	6.02	167.06	0.084	0.105	-0.207	0.079
			I	210.74		0.189		-0.128	
m	H , N_3	3.11	React.	59.24	142.19	0.081	0.069	-0.208	0.046
			I	239.09		0.150		-0.162	

4-methoxy group incurred by the formation of benzylic cation, eq. 1, are plotted against σ^* as presented in Figs. 1 ~ 3 , respectively.



Reactant I (1)

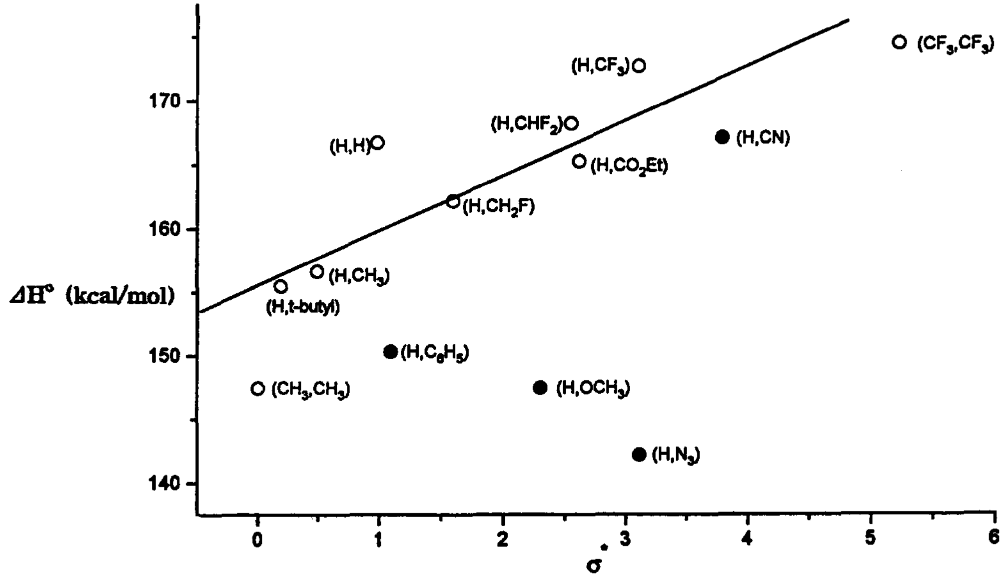


Fig. 1 Plot of ΔH° versus σ^*. (r = 0.872 with slope = 4.490 excepting closed circles, ● ; for π-donors)

Reference to Table 1 reveals that the gas phase ionization of α-substituted benzyl chlorides, eq. 1, is endothermic. Futhermore, examination of Fig. 1 indicates that the endothermicity exhibits an increasing trend as the electron withdrawing power of the α-substituent, σ^*, increases. This is correct reflection of greater destabilization of the carbocation, I , by a stronger electron withdrawing α-substituent, R^1 and/or R^2. Relatively large negative deviations from this trend of changes in ΔH° versus σ^* for R^1, R^2 = H , OCH_3 and H, N_3 suggest that the OCH_3 and N_3 groups have a lesser destabilizing or conversely stabilizing interaction with the cationic center, C_α, due to π donating effect of these groups. Comparison of ΔH_f value for R^1 = R^2 = CH_3 with that of R^1 = R^2 = CF_3

shows that the former is more stable by 26.9 kcal mol^{-1} which is in reasonable agreement with the experimentally estimated value of 23 kcal mol^{-1}. (2a) When the benzyl chloride is heterolyzed to the carbocation, I, and chloride, as in the S_N1 processes, positive charge on C_α increases, $\Delta q(C_\alpha^+) > 0$, in general ; the increment, $\Delta q(C_\alpha^+)$, is seen to decrease, however, linearly with the electron withdrawing power of the α-substituent, Fig. 2. There is an excellent linear correlation (r = 0.996) between $\Delta q(C_\alpha^+)$ and σ^*, if we except 4 π-donors, (H, OCH_3), (H, N_3), (H, CN) and (H, C_6H_5).

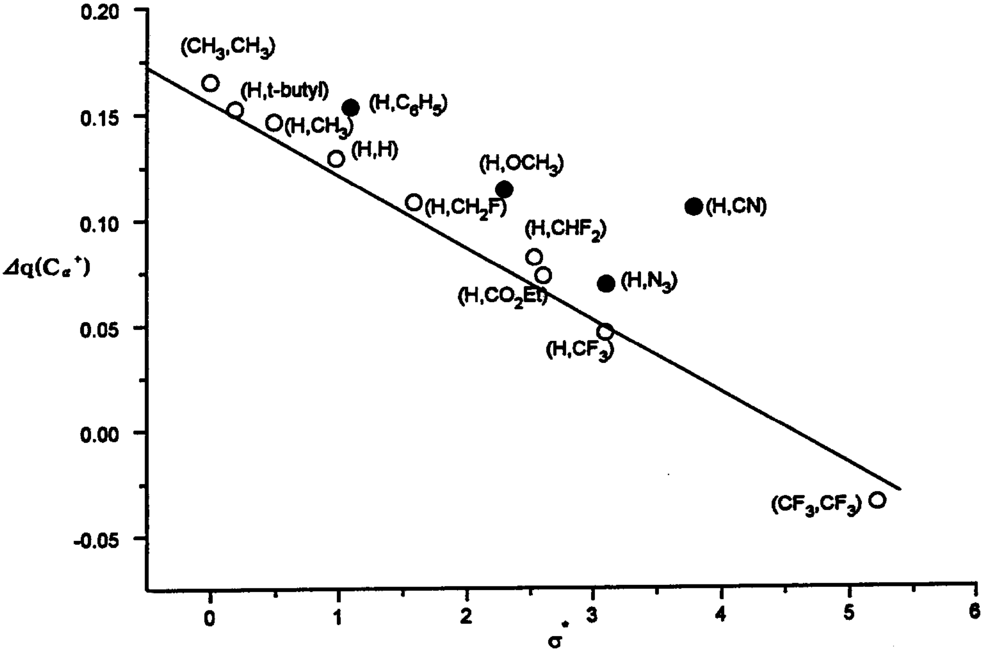


Fig. 2 Plot of $\Delta q(C_\alpha^+)$ versus σ^*. (r = 0.996 with slope = -0.037 excepting closed circles, ● ; for π-donors)

This correlation is a clear demonstration of a linear increase in resonance demand with the increase in the electron withrawing polar effect of the α-substituent ; the resonance interaction with the 4-methoxy ring substituent becomes stronger, delocalizing the positive charge away more strongly from the C_α onto the oxygen, or conversely drawing electrons in more strongly to C_α from the ring and O of the CH_3O group, as the electron withdrawing power of the α-substituent, σ^*, becomes stronger. Since this is a cation stabilizing effect, the thermodynamic destabilization due to the polar effect of α-substituent is partially compensated for, as the reactivity of I observed shows an independence from electron-withdrawing α-substituents.[2a] It is interesting to note that the delocalization of positive charge in the carbocation is so strong for $R^1 = R^2 = CF_3$ that $\Delta q(C_\alpha^+)$ is negative, i.e., the C_α becomes more negative in the carbocation formation, eq. 1.

In contrast to the decrease in the increment of positive charge at C_α , $\delta \Delta q(C_\alpha^+) < 0$, the increment of the positive charge at the oxygen of the 4-methoxy group grows, $\delta \Delta q(O^+) > 0$, with the increase in the electron withdrawing power, σ^*, of the α-substituent. This latter trend is shown in Fig. 3. It is to be noted that the charge increment, Δq, is smaller for the developing positive charge (or decreasing negative charge) on oxygen than that on C_α with α-donors or weak α-acceptors but becomes greater with strong acceptors. Again, excepting 4 π-interacting groups, good linear correlation, r = 0.965, is obtained between $\Delta q(O^+)$ and σ^*. The π-donors show positive deviation in the $\Delta q(C_\alpha{}^+)$ versus σ^* plot, since π-donors partially weaken the electron withdrawing polar effect. These effects of π-interacting groups on $\Delta q(C_\alpha{}^+)$ are exactly reversed in the effects on $\Delta q(O^+)$; π-donors deviate negatively.[5] The effects due to π-interaction of α-substituents supplement the dominant polar effect, σ^*, which is linearly correlated with $\Delta q(C_\alpha{}^+)$ and $\Delta q(O^+)$. The good linearities found for the plots of $\Delta q(C_\alpha{}^+)$ versus σ^* and $\Delta q(O^+)$ versus σ^* suggest that steric effects of R^1 and R^2 groups on the positive charge (or electron) delocalization from the benzylic carbon onto the oxygen through the ring are negligible. This is in agreement with the relatively large resonance demand parameter, advocated by Yukawa and Tsuno[6] in eq. 2, r for the ortho substituted α-t-butylbenzyl compounds.[7]

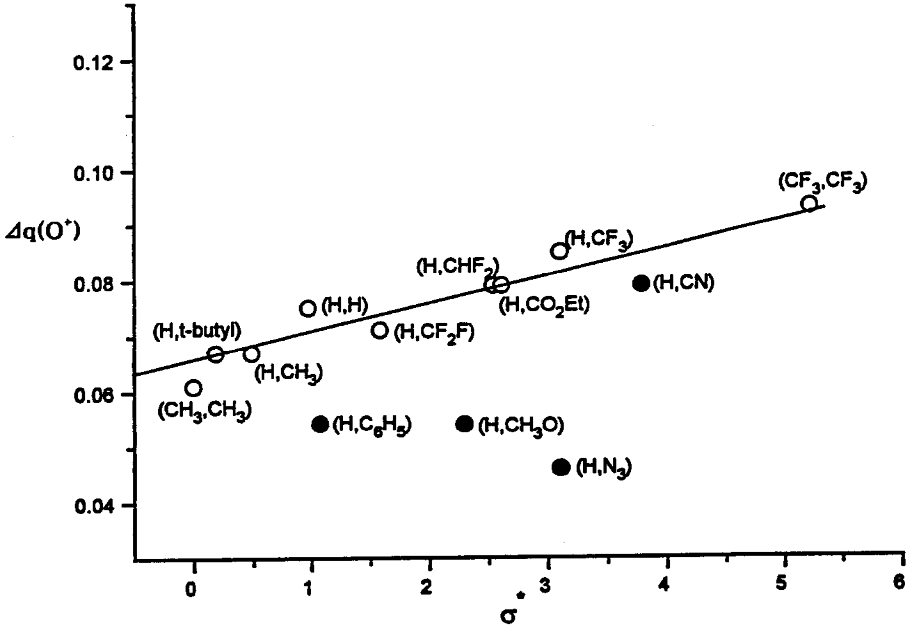


Fig. 3 Plot of $\Delta q(O^+)$ versus σ^*. (r = 0.965 with slope = 0.0057 excepting closed circles, ● ; for π-donors)

$$\log(k/k_0) = \rho\{\ \sigma^0 + r(\sigma^+ - \sigma^0)\ \} \qquad (2)$$

The resonance demand parameter, r, is found to increase with $\Sigma\sigma^*$ of the α-substituents, and the linear correlation between them is also good[8] (for 5 points, r = 0.962 with slope = 0.149).

The r value is based on cumyl system, i.e., for $R^1 = R^2 = CH_3$, $r = 1.0$, which is equivalent to our procedure of using σ^*, since σ^* is zero for the CH_3 group. The experimental ρ^+ values found for the S_N1 solvolytic processes,[9] for which nearly complete carbocation formation is thought to occur in the transition state (equivalent to eq. 2), show relatively lesser sensitibity toward the σ^* value.

In summary, the AM1 studies on the effects of α-substituents show that : (i) Electron-withdrawing polar effect of α-substituents leads to thermodynamic destabilization, $\delta\Delta H^0 > 0$, of benzylic carbocations. (ii) The increments of positive charge on C_α and on methoxy-O accompanying the carbocation formation are linearly correlated with the electron withdrawing polar effect, σ^* ; the positive charge on C_α is more strongly forced away onto the oxygen of the 4-methoxy group by a greater electron withdrawing power of the α-substituent.

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