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ATTENUATION OF α- AND β-METHYL EFFECTS IN THE BROMINATION OF MONO-OLEFINS WITH CONJUGATIVELY ELECTRON-DONATING SUBSTITUENTS.

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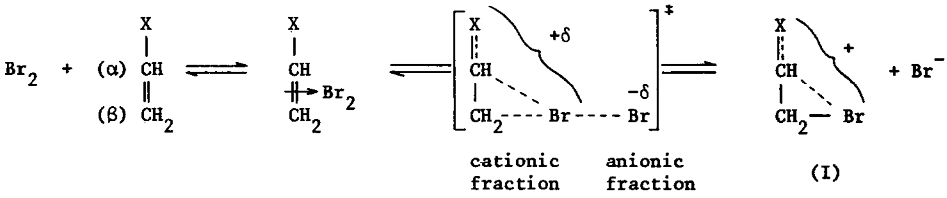
The charge distribution in the substituent-bearing cationic fraction of the transition state is responsible, in part, for the non-additivity of substituent effects in the bromination of 1,1-diarylethylenes (1). In order to show the variation of this charge distribution for the bromination of conjugated mono-olefins, we have determined the rate constants for α- and β-methyl substituted enol ethers and enol esters and compared them with the existing results for alkenes (2) and styrenes (3).

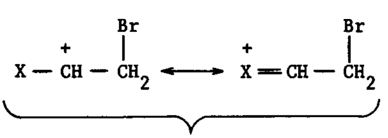
It is generally considered that the rate-determining step of this reaction is the heterolytic fission of the Br-Br bond, leading to a bromo-carbonium ion. This bond breaking is more or less advanced in the transition state, but we can assume that the charge distribution on the cationic fraction of the transition state resembles that in the intermediate ion. So, in the presence of a principal activating group X, conjugated with the double bond, we can write :



(I)

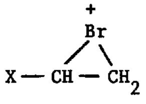
If we compare the compounds X-C(Me)=CH_2 or X-CH=CH-Me with the reference compounds X-CH=CH_2, the α -methyl or β -methyl substituent polar effects are functions of the charge densities on C_α and C_β . The reactivities of the α - and β -substituted compounds, then, depend on two closely related factors : the effect of X on (a) the charge distribution on (I) and on (b) the extent of charge development in the transition state.

In principle, the charge developed can be delocalised, either by X, by means of inductive or conjugative electron displacement, or by neighbouring Br atom assistance ; in particular, a strongly resonant electron-donating X will accentuate (4) the importance of the open carbonium ion (IA) at the expense of the bridged bromonium ion structure (IB) :



$$\underbrace{X-\overset{+}{C}H-\overset{Br}{\overset{|}{C}H_2} \longleftrightarrow \overset{+}{X}=CH-\overset{Br}{\overset{|}{C}H_2}}$$

open carbonium ion
(IA)



bridged bromonium ion
(IB)

Since the charge densities at the two carbon atoms are unlike, α- and β-methyl groups will not have the same effects on the reactivity, and the difference between these effects should be related to the electron-donating ability of X. Furthermore, the delocalisation of charge by X, outside the C_α- C_β vicinity, will tend to reduce the effects of the substituents at these carbon atoms.

The results obtained (Table I), broadly speaking, support these predictions.

Table I : Effect of electron-donating ability of X on the reactivity of α- and β-methyl substituted compounds.

X k	H	Me	Ph	Me-CO-O (5)	Et-O (6)
$k_{X-CH=CH_2}$ (7)	0.50	30.7	67	25.8	5.8×10^6
$\frac{k_{X-C(Me)=CH_2}}{k_{X-CH=CH_2}}$	61	89	87	19	≃ 1.5
$\frac{k_{X-CH=CH-Me}}{k_{X-CH=CH_2}}$ (8)	61	43	2.5	4.9	≃ 1.5
k in l. mol^{-1}. sec^{-1} ; (MeOH ; 0.2 M NaBr ; 25°C)					

The effect of β-Me diminishes with increasing resonance electron donation by X and becomes very small for X=EtO ; this result indicates a marked diminution of the charge at C_β in the transition state. The rate increase, due to the presence of an α-Me, is greatest for

X=Me or Ph, in which cases the charge appears to be more localised on the α-carbon (9). However, for X=Ph, the difference between the α- and β-Me group effects is at a maximum and even larger than what would be expected, compared with X=AcO. For X=EtO, since the reactivity is very large (high resonance contribution), the substituent effects are very weak for both α- and β-positions. We cannot explain this result by considering only charge distribution in (I) : even if the charge were completely localised on the oxygen atom, the α-Me group effect should not be so weak. Moreover, the hypothesis that there is no charge at all on the α-carbon is unacceptable (10).

The second factor (b) which is responsible, in part, for the general tendency for methyl substituent effects to decrease with increasing conjugative electron-donation by X is, namely, the polarity or degree of charge development in the transition state. That such an effect must exist can be seen by considering the analogous slow proton transfer reactions (hydration or hydrolysis in acid media) of ethylenic compounds. Brønsted's α coefficient (which can be obtained by the study of solvent isotope effects or general acid-base catalysis) is generally taken to be a measure of the extent of proton transfer in the transition state. The values of α :

isobutene : $\alpha = 0.9$ (11)
m-chloro α-methylstyrene : $\alpha = 0.7$ (12)
α-methylstyrene : $\alpha = 0.57$ (12)
p-methoxy α-methylstyrene : $\alpha = 0.47$ (12)
ethyl vinyl ether : $\alpha = 0.6$ (13)

show much the same trend as has been noted above for the methyl substituent effects. The results for α-methylstyrenes are particularly striking : the most activating substituent gives rise to the earliest transition state. So, the very weak substituent effects on enol ether reactivity indicate little charge development in the transition state, that is, the C-Br bond is formed to only a small extent.

This analysis of the bromination kinetics of such different compounds as alkenes and enol ethers, can only be considered as a tentative step towards an understanding of substituent effects. More detailed studies are in hand, in particular on ring-substituted α- and β-methyl styrenes, which we hope will provide a more quantitative interpretation.

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It is reasonable to suppose, either the existence of an unique ion, which should be intermediate between the ions (IA) and (IB), or the formation of two ions (IA) and (IB) along two different reaction paths, one of them being prefered. However, the discussion should remain valid whatever assumption is made.

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