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KINETIC SALT EFFECTS ON BROMINATION OF ETHYLENIC COMPOUNDS. COMPETITION BETWEEN ELECTROPHILIC Br_3^- AND NUCLEOPHILIC ASSISTANCE BY Br^-.

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The electrophilic reactivity of the tribromide ion (Br_3^-) in bromination reactions is a long standing problem. A number of mechanisms, associated with the presence of both bromine and bromide ions, have been proposed :

- catalysis by Br^- (1-5) ,
- electrophilic reactivity of Br_3^- (1,6-8) ,
- nucleophilic reactivity of Br_3^- (1,3) .

None of these mechanisms is really satisfactory to account for the whole body of experimental results.

We reinvestigated this problem as a particular case of general kinetic salt effects (9).

Assuming that a salt may have two kinetic effects,

- a salt-induced medium effect (ES_M) (9,10) ,

$$\log (k/k_0) = a\left[\text{salt}\right] , \tag{1}$$

- an assistance effect (ES_A) (9),

$$k = k_0 \left(1 + \frac{k_{salt}}{k_0}\left[\text{salt}\right] \right) , \tag{2}$$

the simplest reaction scheme for bromination in the presence of Br^- is written as follows :

$$\begin{aligned} Ol + Br_2 &\xrightarrow{k_{Br_2}} P \\ Ol + Br_2 + Br^- &\xrightarrow{k_{Br^-}} P \end{aligned} \tag{3}$$

The variation of the overall rate constant (k_g) as a function of Br^- concentration is given by

(4) $$\frac{k_g(1 + K[Br^-])}{k_{Br_2}} = 1 + B[Br^-]$$

where the term ($1 + K[Br^-]$) allows for the secondary effect of the equilibrium

(5) $$Br_2 + Br^- \overset{K}{\rightleftharpoons} Br_3^-$$

According to scheme (3), the catalytic coefficient "B" can be expressed by equation (6) :

(6) $$B_{Br^-} = a + \frac{k_{Br^-}}{k_{Br_2}}$$; a = coefficient of the exponential of the ES_M effect on k_{Br_2}.

The curve of figure I illustrates the existence of a correlation between the reactivity ($\log k_{Br_2}$) of 31 ethylenic compounds and their catalytic coefficient B as defined in eq.6 . Neglecting the small contribution from the "a" coefficient of the ES_M effect (9), the curve of figure I is due to the variation of the ratio k_{Br^-}/k_{Br_2} as a function of reactivity .

Such a curve, with inversion of slope, can only be interpreted in terms of two competing mechanisms associated with bromide ions . We suggest these two mechanisms to be :

- electrophilic attack by Br_3^- on the substrate ,($B_{Br_3^-} = a + \frac{Kk_{Br_3^-}}{k_{Br_2}}$) ,
- nucleophilic assistance of Br^-, namely slow attack by Br^- on the charge transfer complex between bromine and ethylenic compounds (11),(B_{Br^-} = eq. 6).

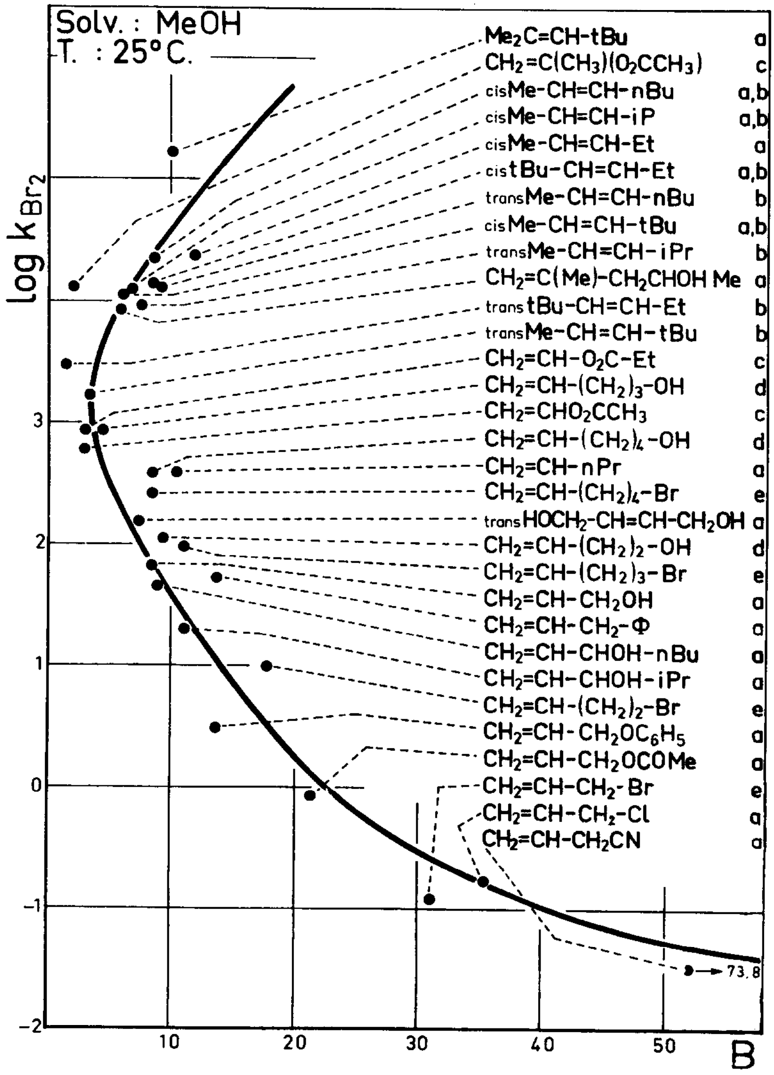
The former mechanism predominates at high reactivity, the latter at low reactivity .

This scheme and the corresponding expression of the overall rate constant ,

(7) $$k_g = \frac{k_{Br_2} + (k_{Br^-} + Kk_{Br_3^-})[Br^-]}{1 + K[Br^-]}$$ (12)

account for the results of N.P.Kanyaev (4) and K.Yates (8) who found a monotonic relation between the reactivity and the ratio $k_{Br_3^-}/k_{Br_2}$, where $k_{Br_3^-} > k_{Br_2}$.

Figure I . Correlation " Reactivity - Sensitivity to assistance effect by Br^- " illustrating a dual mechanism associated with Br^-.



(a): Ref.(5); (b):this work; (c):Ref.(13); d:Ref.(14); e:Ref.(15).

These second order rate constants ($M^{-1}.s^{-1}$) have been measured by various methods (coulometric concentrostat(this work,(5)),potentiometry(5,13-15) and amperometric titrations(5,15)) under the same conditions : very low concentration of reactants (TFCR) and excess of salt (EXSEL) .

These results correspond, in fact, to the predominance of the assistance effect of bromide ions over the electrophilic additions of both Br_2 and Br_3^- ; the reactivity of Br_3^- being always lower than that of Br_2 .

We think that this study is the first to provide both clear evidence of the dual mechanism associated with the bromide ions in bromination and a good assessment of the relative electrophilicities of Br_2 and Br_3^- over a range of reactivity of 10^7 .

Further studies on kinetic salt effects are in progress to ascertain the assistance effect of anions and the overall reaction scheme for bromination .

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