

ENOL ETHER IODINATION : POLARITY OF THE TRANSITION STATE

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(Received in UK 17 July 1972; accepted for publication 27 July 1972)

In the context of our studies on the reactivity of conjugated olefins (1) and, in particular, in order to compare the reactivities of enols (2) and enol ethers, we have developed an original kinetic study of the iodination of very reactive enol ethers. We report some preliminary results concerning  $\alpha$ - and  $\beta$ -alkyl substituent effects on the reaction in water, as well as the effect of change of solvent composition in water-methanol mixtures, in order to determine the structure and the polarity of the rate determining transition state (TS).

By analogy with the bromination of unsaturated compounds, both iodine molecules and triiodide ions can be considered as competing iodinating species, with elementary rate constants  $k_{I_2}$  and  $k_{I_3^-}$ . The salt effect of the added iodide ion should then follow the equation :

$$k_g ( 1 + K_{I_3^-} [I^-] ) = k_{I_2} + k_{I_3^-} K_{I_3^-} [I^-] \quad (1)$$

where  $k_g$  is the overall iodination rate constant based on the analytical iodine concentration variation  $[I_2]_a = [I_2] + [I_3^-]$ , and  $K_{I_3^-}$  the equilibrium constant for the triiodide ion formation (3).

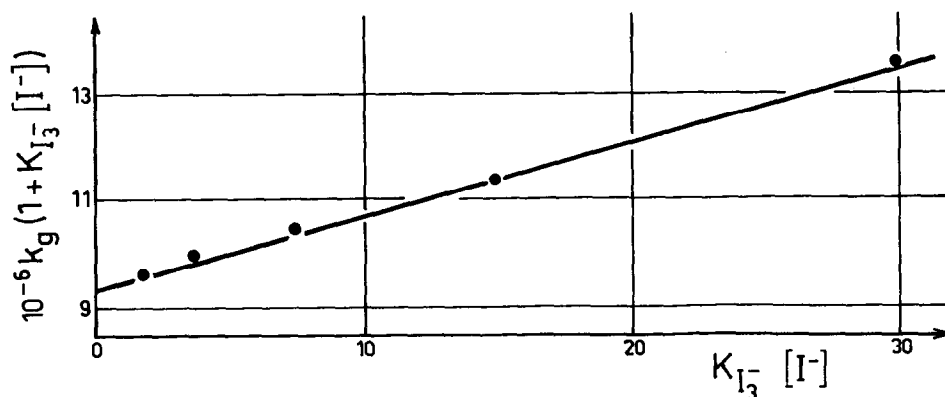


Fig.- Variation of overall second order rate constants for iodination at 25°C of ethyl vinyl ether in water with added iodide ion.

The figure shows that equation (1) is valid for ethyl vinyl ether and allows us to separate the two very high elementary rate constants :

$$k_{I_2} = (9.4 \pm 0.4) \times 10^6 \text{ M}^{-1} \text{ sec}^{-1} \quad \text{and} \quad k_{I_3^-} = (1.3 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$$

$$I_3^- \text{ is much less reactive than } I_2 \text{ ( } k_{I_2} / k_{I_3^-} \approx 70 \text{ )}$$

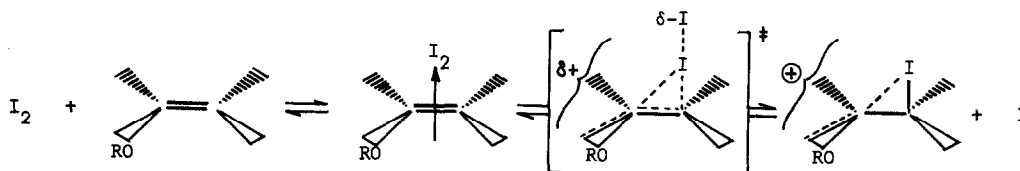
The substituent effects observed (table) in aqueous media (effects of an  $\alpha$ - or cis  $\beta$ -alkyl substitution) are markedly greater than those observed previously for the bromination of the same ethers in methanol (1) (a factor of 1.5 for an  $\alpha$ - or  $\beta$ -methyl substitution) and greater than those expected for this latter reaction in aqueous media (4).

TABLE : Effects of  $\alpha$ - and  $\beta$ -alkyl substitution on the iodination rate constants for enol ethers.

enol ethers	$10^{-6} k_g$ (a)	$k_{I_2}$ (rel.) (6)
EtO - CH = CH <sub>2</sub>	0.44	1
EtO - C(Me) = CH <sub>2</sub>	6.4	14.5
EtO - CH = CH - Et ( <u>cis</u> )	2.2	5.0
EtO - CH = CH - Et ( <u>trans</u> )	0.36	0.8

(a)  $k_g$  in  $\text{M}^{-1} \text{sec}^{-1}$  (water;  $4 \times 10^{-2}$  M NaI; 25°C) determined by coulometerometry (5).

As in the case of bromination, it seems reasonable to assume that the rate determining step of iodination is the heterolytic fission of the I-I bond, leading to a cationic intermediate (an  $\alpha$ -iodo oxocarbenium ion, more or less stabilised by neighbouring halogen assistance) accompanied by the formation of iodide ion specifically solvated by hydrogen bonding (1,7).



We formerly attributed the very small structural effects observed in the bromination of enol ethers (1) to two factors : (a) a partial delocalisation of the positive charge by the oxygen atom and (b) a low degree of charge development in the TS. For iodination, on the other hand, the larger structural effects can be interpreted in terms of a more polar TS if it is accepted that the rate increase caused by  $\alpha$ - and cis  $\beta$ -alkyl substitution is related to the charge densities at the C <sub>$\alpha$</sub>  and C <sub>$\beta$</sub>  atoms in the TS.

A measure of the TS polarity in the bromination of 1-pentene was obtained by studying the solvent effect in methanol-water mixtures on the rate constant in relation with the TS solvation (7). From preliminary results at 25°C, in water-methanol 50/50 w/w, for iodination of ethyl vinyl ether ( $k_g = 6 \times 10^4$ ,  $1.1 \times 10^5$  and  $4.5 \times 10^5 \text{ M}^{-1} \text{sec}^{-1}$  for  $[\text{INa}] = 2 \times 10^{-2}$ ,  $10^{-2}$  and  $2 \times 10^{-3} \text{ M}$ ), one deduces :

$$k_{I_2} \approx 4.6 \times 10^5 \text{ M}^{-1} \text{sec}^{-1} \quad (8)$$

This value is lower than  $k_{I_2}$  (water) by a factor of 20, which corresponds to a difference of 1.8 kcal/mol on the activation free energy  $\Delta G^\ddagger$ . If one neglects the much less important cationic part solvation, this effect can be attributed, in first approximation, to the difference in the solvation energies of leaving iodide ion (charge  $\delta^-$ ) in TS. The transfer energy of the iodide ion from water to such a 50% mixture has been estimated to be 3.28 kcal/mol (9) (this expresses the difference in solvation of  $I^-$  in the two solvents). This comparison shows that in the TS the energy of solvation of  $I^{\delta-}$  corresponds roughly to half that of the solvation of a free iodide ion, which implies a large degree of charge development.

Since for hydrolysis of analogous enol ethers, which is a rate determining electrophilic proton addition (10), it is considered that the proton is about half-transferred in TS ( $\alpha = 0.6$  for ethyl vinyl ether (10c)), it is reasonable to think that the charge on the oxocarbenium part of the TS is of the same order of magnitude for the additions of iodine and of a proton. Therefore, the  $\alpha$ - and  $\beta$ -alkyl group effects for iodination can be compared, in magnitude and in direction, to those on the corresponding catalytic rate constants ( $k_{H_3O^+}$ ) for hydrolysis of analogous enol ethers :

MeO - CH = CH <sub>2</sub>	$k_{H_3O^+} \approx$	1	$\text{M}^{-1} \text{sec}^{-1}$	(10d)
MeO - C(Me) = CH <sub>2</sub>	" =	970	"	(10a)
MeO - CH = CH - Me ( <u>cis</u> )	" =	0.25	"	(10b,d)
MeO - CH = CH - Et ( <u>cis</u> )	" =	0.33	"	(10b)
MeO - CH = CH - Et ( <u>trans</u> )	" =	0.10	"	(10b)

- the  $\alpha$ -alkyl group effect is much weaker for iodination than for protonation ;
- in opposition to hydrolysis, there is no diminution of  $k_{I_2}$  for a cis  $\beta$ -alkyl substitution (11) ;
- so, the difference between  $\alpha$ - and cis  $\beta$ -effects is smaller for iodination.

These remarks suggest that the cationic part of the TS must have less carbonium character for iodination than for hydrolysis, and this would be attributed to  $\alpha$ -iodine atom participation in charge delocalisation (12). The absence of a dominant hyperconjugative effect, which is

responsible in protonation (13) for the rate decrease caused by a  $\beta$ -alkyl substitution is, from this point of view, significant (for hydrolysis, this rate decrease is attributed to a carbonium ion destabilisation due to the diminished hyperconjugative effect).

Thus our kinetic results argue in favour of a more polar TS for iodination than for bromination, with the cationic part resembling an  $\alpha$ -iodo oxocarbenium ion in which the charge is strongly delocalised by the  $\alpha$ -iodine atom despite competing resonance stabilisation by the ethoxy group.

Acknowledgment : Technical assistance provided by Mr A. ADENIER is gratefully acknowledged.

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