REACTIVITY OF THE ENOLS OF SATURATED ALIPHATIC KETONES:

QUASI-IDENTITY OF THE RATE CONSTANTS FOR BROMINATION AND IODINATION

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The identity of the <u>apparent</u> rates of different halogenations of ketones in acidic media is considered to be one of the essential proofs of the enol mechanism; it is then accepted that halogen addition to the enol is much faster than enolisation. <u>When however this addition is slow</u>, that is at very low halogen concentrations, is there really a significant difference in the halogenation second order rate constants with iodine, bromine and chlorine (1)?

Under the conditions used in this study, the two steps, enolisation and halogen addition to the enol, have comparable rates; the two experimentally obtained constants are the following (2): the enolisation rate constant (k_1) and the apparent overall halogenation rate constant $((k_{II})^{X_2}_g)$ which is defined in terms of variations of the analytical halogen concentration $[X_2]_a = [X_2] + [X_3^-]$. The constant $(k_{II})^{X_2}_g$ includes the keto-enol equilibrium constant:

$$(k_{II})^{X_2}_g = K_E \cdot (k_{X_2})_g \quad [1] \; ; \; K_E = k_1/k_{-1} \quad [2]$$

The corresponding mechanism is:
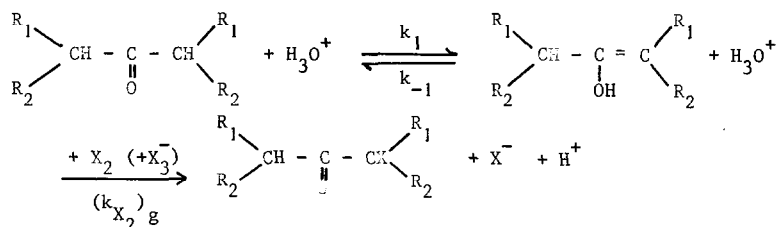
As in the case of addition to an alkene, it is presumed that in the presence of halide ion, the halogen reacts either free or as trihalide ion X_3^- (equilibrium constant $K_{X_3^-}$). If K_E is considered to be independent of the halide ion concentration:

$$(k_{II})_g^{X_2} = \frac{k_{II}^{X_2} + k_{II}^{X_3^-} \cdot K_{X_3^-} \cdot [X^-]}{1 + K_{X_3^-} \cdot [X^-]} \qquad [3]$$

The determination of the constants $k_{II}^{Br_2}$ and $k_{II}^{I_2}$, for the bromination and the iodination by free bromine and iodine of the same ketone (fig), enables us to compare the reactivity of a given enol with molecular bromine and iodine:

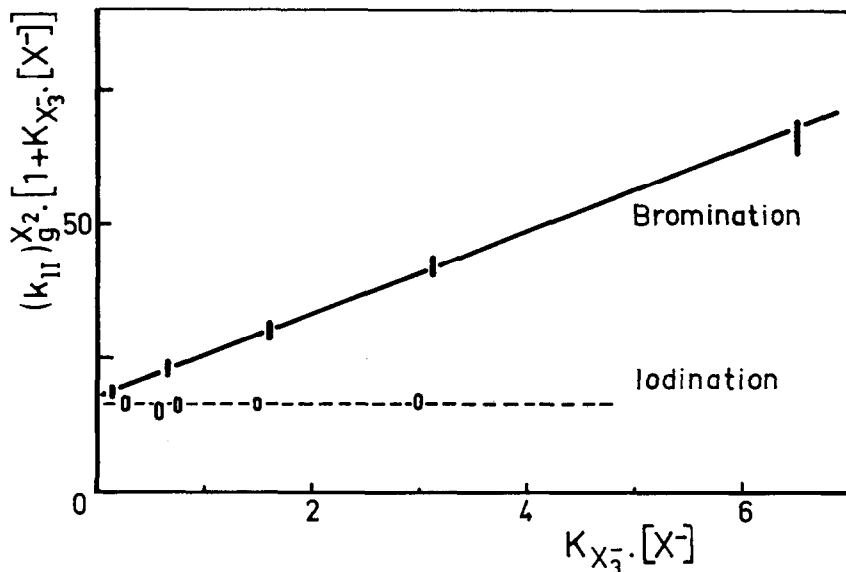$$\frac{k_{II}^{Br_2}}{k_{II}^{I_2}} = \frac{k_{Br_2}}{k_{I_2}} \qquad [4]$$

Fig. Apparent overall second order rate constant for bromination and iodination of the enol of acetone (25°C) vs halide concentrations.

$$K_{Br_3^-} = 16,3 \ (3) \qquad \text{and} \qquad K_{I_3^-} = 751 \ (4)$$

TABLE :

Apparent rate constants for bromination of enols
of saturated aliphatic ketones. (25°C)   (5).

Enol	Br_2 k_{II} (M.$^{-1}$ sec.$^{-1}$)	Br_3^- k_{II} (M.$^{-1}$ sec.$^{-1}$)	I_2 k_{II} (M.$^{-1}$ sec.$^{-1}$)
$CH_3 - C(OH) = CH_2$	17.7 ± 1 (a)	7.7	16.6 ± 1 (a)
$CH_3 - CH_2 - C(OH) = CH - CH_3$	105 ± 7 (b)	49	108 ± 8 (a,b)
$(CH_3)_2CH - C(OH) = C(CH_3)_2$	44 ± 3 (b)	23	49 ± 3.5 (b)

(a) : $[H_2SO_4] = 0.1$ M   (b) : $[H_2SO_4] = 0.5$ M
Ketone concentration $\underline{ca}$. 10^{-2} M
Initial analytical bromine or iodine concentrations = $10^{-5} - 5.10^{-7}$ M
depending on the halide ion concentration.

Two important results emerge from our measures:
(a) Whereas iodination takes place by free iodine only (no I_3^-) the dependence of $(k_{II})_g^{Br_2}$
upon bromide ion concentration can be interpreted in terms of Br_3^- acting as a brominating
species. For these three ketones, the ratio of the elementary rate constants $k_{Br_2}/k_{Br_3^-}$ is
low (ca. 2) (6), constant, and of the same order of magnitude as that observed for
the most reactive alkenes (7).

(b) For the three enols studied here $k_{II}^{Br_2} = k_{II}^{I_2}$, i.e., the elementary rate constants for bromi-
nation and iodination are approximatively identical. This very surprising result could be
explained by diffusion controlled kinetics: the elementary constants are seen to be very large
if the very low value of K_E is taken into account. However, the bromination rate constant (k_{Br_2})
has been estimated at 10^7 M^{-1} sec^{-1} for acetone enol, by direct measurement (8), or indirec-
tely, if K_E (ca. 10^{-6}) is taken in account (9,10). Thus the value of k_{Br_2} is below that predic-
ted for diffusion control (11). Two doubts remain however: firstly, K_E may be lower than es-
timated (particularly in dilute solution)(10); secondly, there is some uncertainty about the
limit diffusion rate constant value for such a complex reaction (the only measured rate limits
are for proton transfer reactions and free radical recombination). The possibility of diffusion
control is, therefore, not entirely to be excluded.

The results obtained here are to be compared with those of BELL and al.
(9,12) who observed that k_{Cl_2} is about 8 times lower than k_{Br_2} for acetone enol under similar
conditions. The small difference in the reactivity of these halogens and their relative order
are unlike what is observed for the alkenes (13). Generally, the differences in reactivity of
halogens for additions to ethylenic double bonds can be interpreted in terms of the energies
of the X - X and C - X bonds which are partially broken and formed in the transition state,

the solvation energies of the leaving halide ion, and the ability of the halogen as a neighbou-
ring group to stabilise a positive charge. It is then beyond question that these differences in
halogen reactivity depend on the degree of charge development at the level of the transition
state (14). In the case of enols, if the reaction is not diffusion controlled, the small
reactivity differences between the halogens and, in particular between bromine and iodine, could
indicate that the transition states correspond to low charge development. Essentially the same
conclusion was reached in interpreting the small effects of α- and β-methyl substituents on
the rates of bromination of enol ethers (15).

<div align="center">REFERENCES</div>

1) Such a difference could be expected from kinetic results on the halogenation of different
   ethylenic compounds (see ref. 13).

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5) The enolisation rate constants (see following paper) are very nearly identical with the
   litterature values: this implies good separation of the two constants k_I and k_{II}, and
   justifies the mechanism and the rate equation (which assumes, in particular, a steady state
   enol concentration).

6) a) The results for acetone are very close to those obtained by BELL and DAVIS (see ref 9).
      In view of the experimental uncertainity, their value of $k_{Br_2}/k_{Br_3}-(= 4)$ is not necessarily
      in contradiction with ours. Despite a possible effect of ionic strength, which was not
      controlled here, our result appears more likely to be correct since we have varied the
      bromide concentration over a much greater range.

   b) In the experimental conditions, those ketones iodination is practically irreversible
      (very low α-iodinated ketone formation and very weak iodide concentration).

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14) Halogenation of an ethylenic double bond may be considered to proceed by an $Ad_E Cl$ mechanism
    (see F. GARNIER and J.E DUBOIS, Bull. Soc. Chim. Fr., 3797 (1968)), i.e., initial formation
    of a charge transfer complex, followed by slow heterolysis of the X - X bond, accompanied
    by formation of the covalent C - X bond (see ref. 15).

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