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REDUCTION OF DIMETHYLSULPHOXIDE BY IODIDE IONS IN AQUEOUS PERCHLORIC ACID

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The reduction of some alkylsulphinylcarboxylic acids by iodide ions in aqueous solution has been studied by Allenmark (1). According to this author the reaction is catalysed by acids and the rate coefficients are almost independent of iodide ion concentration; furthermore, the carboxylic group is involved in the rate determining step.

In the course of an independent work some of us studied the reduction of a number of aliphatic and aromatic sulphoxides in diluted acetic acid (2), and found an acid catalysis together with a definite dependence of rate coefficients on iodide ion concentration and on steric environment of the sulphoxide group.

The discrepancies between these results, due largely, in our opinion, to differences in the substrates as well as in the reaction medium, suggested that a reinvestigation of the problem should be undertaken.*

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* Very recently a paper appeared by J.H. Krueger (3) on the reduction of aqueous DMSO (75 to 98.5%) by iodide ions. For the high concentration of DMSO, Krueger's results are not directly comparable with Allenmark's and ours.

In this communication we wish to report the first results of this investigation; further results will be reported on later.

The kinetic of the reduction of dimethylsulphoxide (DMSO) by iodide ions (added as NaI) in water - perchloric acid (3 to 7 M) has been studied. All the reactions have been run under nitrogen, in the presence of a large excess of sodium iodide, to avoid reversibility (1,2) and to have first-order kinetics. In these conditions regular first-order kinetics up to 70-80% of reaction have been always observed.

The results are reported on in tables 1, 2 and 3, and show that:

i) the reaction is acid-catalysed (table 1): a satisfactorily linear correlation between log k and H_o is found, with a slope of 1.22;

ii) the pseudo-first-order coefficients increase with iodide ion concentration (table 2): slopes of log k / log$[I^-]$equal to 1.2 at$[HClO_4]$3.88 M, and to 1.4 at$[HClO_4]$5.99 M may be calculated;

iii) the reaction presents a slight positive salt effect (table 3) *

A correct analysis of the results presented above requires an evaluation of the salt effect on H_o and on reaction rates. The technique of running the reactions at constant ionic strength is not completely valid in this case, as different ions affect H_o differently (4). Moreover, direct measurement of the effect of iodide ions on H_o is disturbed by the easy oxidability of I^-.

Therefore, at this stage of the investigation, we preferred to use a

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* The salt affects the rates through its effect on H_o and through a positive kinetic effect. When the effect on H_o is allowed for, a linear correlation between the logarithm of rate coefficients and the logarithm of salt concentration is found.

rough evaluation of these "salt effects", taking as our basis that of sodium chloride on H_o at the perchloric acid concentrations used in the kinetic runs (see table 2).

When the second-order rate coefficients (k', table 2) are corrected for the effect of iodide ion concentration on H_o, a slope slightly higher than 1 for the plots of log k / log$[I^-]$ may be calculated for both the reaction series; in fact the values of log k' + H_o (table 2) are almost constant with increasing $[I^-]$.

The slight increase observable in the log k' + H_o values might be due to the positive salt effect (see table 3). However further refinements seem unjustified as, probably, a larger error is made in taking the salt effect of Cl^- on H_o to be equal to that of I^-.

On the other hand, the rate of reduction of DMSO in water appears to be much slower than those of the alkylsulphinylcarboxylic acids reported by Allenmark. It confirms his hypothesis of a specific participation of the carboxylic group when it is in a favourable steric environment.

We feel that reduction of the sulphinyl group assisted by the carboxylic group may follow a mechanism quite dissimilar from that of non-assisted reduction, and that may be the cause of differences in the kinetic features as well as in the hypothesis advanced by the two groups of workers.

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TABLE 1

First-order rate coefficients at 25.0° for the reaction of DMSO with iodide ions in aqueous perchloric acid

$[DMSO] = 1.0 \times 10^{-2}$ M ; $[I^-] = 30 \times 10^{-2}$ M

$[HClO_4]$ M	$k \times 10^4$ (sec^{-1})	$-H_o$*
2.91	0.165	1.19
3.88	1.1	1.65
4.85	4.31	2.15
5.82	24	2.72
6.79	113	3.44

* The H_o values refer to solutions of perchloric acid in the absence of salt.

TABLE 2

Influence of iodide ion concentration on the first-order rate coefficients

$[DMSO] = 1.0 \times 10^{-2}$ M in water, at 25.0°

$[HClO_4]$ M	$[I^-] \times 10^2$ M	$k \times 10^4$ (sec^{-1})	$k'(k/[I^-]) \times 10^4$ ($sec^{-1} mol^{-1}$ l)	$-H_o$*	$-(\log k' + H_o$
3.88	-	-	-	1.65	-
3.88	20	0.66	3.3	1.68	5.17
3.88	30	1.1	3.67	1.71	5.14
3.88	40	1.6	4.0	1.73	5.13
3.88	50	2.08	4.16	1.75	5.13
5.99	-	-	-	2.85	-
5.99	20	15.9	79.5	2.90	5.00
5.99	30	26	86.6	2.93	4.99
5.99	40	41.7	104.2	2.97	4.95

* The H_o values refer to solutions containing NaCl in concentrations equal to those of I^-.

TABLE 3

Salt effect ($NaClO_4$) on the first-order rate coefficients
[DMSO] = 1.0 x 10^{-2} M ; [I^-] = 30 x 10^{-2} M ; [$HClO_4$] = 3.88 M in water, at 25.0°

[$NaClO_4$] x 10^2 M	-	30	60
k (sec^{-1}) x 10^4	1.1	1.94	2.36

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