On the Mechanism of Cathodic Cleavage of β-Keto-sulphones

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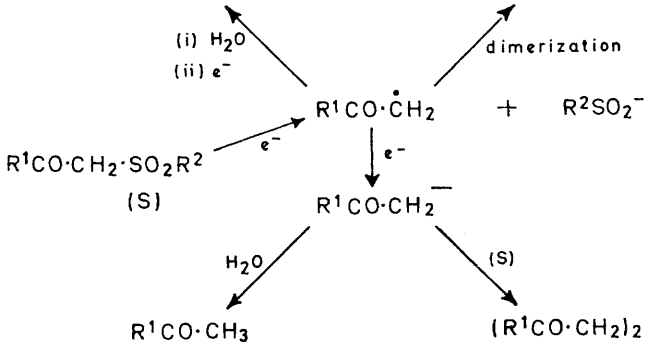
Summary γ-Diketones, obtained as by-products in the electrolytic cleavage of β-keto-sulphones at a mercury cathode, have been demonstrated to form *via* radical dimerization rather than nucleophilic displacement.

THE cathodic cleavage of β-keto-sulphones has recently been described.[1] It was found that on electrolysis at a mercury cathode in dimethylformamide–water (10 : 1 v/v), monoketones were the main products (see Scheme). Varying amounts of γ-diketones were also obtained *via* a postulated dimerization of the radicals initially formed.



SCHEME

The extent of dimerization was influenced by the choice of supporting electrolyte. For example, in the reduction of p-MeO·C_6H_4·CO·CH_2·SO_2Me, the yield of dimer was 20% with lithium toluene-*p*-sulphinate present in the electrolyte and 42% with tetrabutylammonium toluene-*p*-sulphinate.

An explanation of the influence of the cationic part of the supporting electrolyte upon the product distribution was suggested,[1] namely, the different degree of solvation of the cations. The same argument has been used by Baizer and his co-workers[2,3] to account for the fact that the cathodic hydrodimerization of acrylonitrile is favoured by the presence of quaternary ammonium ions in the catholyte.

An alternative to the radical dimerization might, however, be invoked for the reaction leading to γ-diketones. The initial cleavage of the β-keto-sulphone might be a two-electron process (*i.e.*, two successive one-electron transfers with no intervening chemical step). The carbanion $R^1CO{\cdot}CH_2^-$ (see Scheme) thus formed might act either as a base towards water to yield $R^1CO{\cdot}CH_3$ (or its enolic form) or as a nucleophile towards the substrate $R^1CO{\cdot}CH_2{\cdot}SO_2R^2$ to yield $(R^1CO{\cdot}CH_2)_2$.

The suggestion of a solvation difference to explain the product distribution is also applicable to the heterolytic mechanism. The carbanion $R^1COCH_2^-$ is formed in a region close to the cathode, where absorption of cations, particularly tetrabutylammonium ions, may be expected to be important, and the carbanion, being a very short-lived species will not diffuse away from this region before it has reacted. In consequence, the reaction with water to give the monoketone is suppressed when tetrabutylammonium ion is present.

An argument against the heterolytic mechanism may be obtained from a comparison of the results found[1] with *p*-$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}SO_2Me$ (57% ketone, 20% dimer isolated) and *p*-$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}SO_2Ph$ (92% ketone, no dimer isolated). Since $PhSO_2^-$ may be expected to be at least as good a leaving group as $MeSO_2^-$, it is hard to see why less dimer is formed with the phenyl sulphone than with the methyl sulphone, if an S_N2 reaction is operating.

A more decisive experiment has now been carried out.† An approximately equimolar mixture of two β-keto-sulphones with different reduction potential ($PhCO{\cdot}CH_2{\cdot}SO_2Me$: $E = -1{\cdot}50$ v, $Me[CH_2]_5CO{\cdot}CH_2{\cdot}SO_2Ph$: $E = -1{\cdot}75$ v; E = potential used in preparative runs; see ref. 1) was electrolysed at a potential at which only one of the compounds was attacked ($-1{\cdot}50$ v *vs.* S.C.E.). The electrolysis was continued until all of the reducible component had been consumed. The symmetric γ-diketone from the latter compound was exclusively formed; none of the mixed diketone was present. If an S_N2 attack of a carbanion on the substrate had been the route of formation of the γ-diketone, it is hard to see why no mixed product was formed. We therefore conclude that the γ-diketones are formed by dimerization of radicals.

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[1] B. Lamm and B. Samuelsson, *Acta Chem. Scand.*, 1970, **24**, 561.
[2] J. P. Petrovich, J. D. Anderson, and M. M. Baizer, *J. Org. Chem.*, 1966, **31**, 3897, and previous publications in this series.
[3] M. M. Baizer, *J. Electrochem. Soc.*, 1964, **111**, 215.