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MECHANISM OF REACTIONS OF α-DIAZOSULPHONES
ACID-CATALYSED HYDROLYSIS OF p-METHOXYPHENYLSULPHONYL DIAZOMETHANE

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Recently α-diazosulphones[1] which are a new type of diazo compounds, were prepared by Strating and Van Leusen[2]. It is worthwhile to compare the reactivity of these compounds with that of other types of diazo compounds. Therefore, p-methoxyphenylsulphonyl diazomethane (I) was subjected to acid-catalysed hydrolysis, and the mechanism of this reaction investigated more closely. The reaction occurring is similar to that of diazoketones.

$$\underset{\text{I}}{p\text{-}CH_3OC_6H_4SO_2CHN_2} + H_3O^{\oplus} \longrightarrow \underset{\text{II}}{p\text{-}CH_3OC_6H_4SO_2CH_2OH} + N_2 + H^{\oplus}$$

Presumably, the reaction product II[3] is partly dissociated into formaldehyde and p-methoxybenzenesulphinic acid.

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[1] The name diazosulphones is also used for compounds of the type RSO_2-N=N-R, see: C.D.Ritchie, J.D.Saltiel and E.S. Lewis, J.Amer.Chem.Soc. **83**, 4601 (1961).

[2] J.Strating and A.M.van Leusen, Rec.trav.chim. **81**, 966 (1962).

[3] Product II (m.p.83-85°) was prepared analogous to the procedure for phenyl hydroxymethyl sulphone given by H.Bredereck and E.Bäder, Chem.Ber. **87**, 129, 784 (1954). These authors already mentioned the tendency of this type of compounds to dissociate.

The rate of the reactions can be determined by measuring the amount of nitrogen evolved or, more conveniently, by following the absorbance at a suitable characteristic wavelength of compound I, i.c. either at 397 mμ ($\varepsilon \sim 100$) or at 258 mμ ($\varepsilon \sim 12500$).

In 40% dioxane-water as solvent the hydrolysis catalysed by perchloric acid appeared to be first order with respect to the α-diazosulphone. In the concentration range from 0.2 up to 1.0 N perchloric acid the reaction rate in this solvent follows the Hammett acidity function[4] H_0, the plot of log k_1 against $-H_0$ having a slope of 1.13 at 25°.

Information about the mechanism was obtained from experiments in dioxane-deuterium oxide. The magnitude of the kinetic isotope effect[5], k_D/k_H, of 3.3 indicates specific hydrogen ion catalysis.

$$\underset{\text{I}}{p\text{-}CH_3OC_6H_4SO_2CHN_2} + H_3O^{\oplus} \rightleftarrows \underset{\text{III}}{p\text{-}CH_3OC_6H_4SO_2CH_2N_2^{\oplus}} + H_2O$$

Confirmatory evidence about the fast pre-equilibrium which is inherent to this kind of catalysis, was obtained from H-D exchange experiments. After 15% hydrolysis in 0.1 N perchloric acid in 40% dioxane-deuterium oxide, the reaction mixture was neutralised, extracted with carbon tetrachloride and analysed by NMR. No characteristic peak due to the $-CHN_2$ proton was observed. Consequently, complete H-D exchange had taken place.

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[4] C.A.Bunton, J.B.Ley, A.J.Rhind-Tutt and C.A.Vernon, J.Chem.Soc. 2327 (1957).

[5] C.A.Bunton and V.J.Shriner, J.Amer.Chem.Soc. **83**, 42, 3207, 3214 (1961).

The next question is whether the diazonium ion III decomposes unimolecularly (A-1), yielding the carbonium ion IV, or loses nitrogen simultaneously with the attack of a nucleophile in a bimolecular step (A-2). Accepting the Zucker-Hammett hypothesis[6] the former possibility seems to be most likely because of the linear relationship of log k_1 and $-H_o$ as mentioned above. Also supporting an A-1 mechanism is the observation that at the same acid concentration the reaction rates are approximately proportional[7] with h_o going from 60% to 40% dioxane-water. Thusfar, it has not been possible to follow the reaction in water at acid concentrations high enough to permit application of Bunnett's theories[8]. According to Taft and coworkers[9] the slightly negative entropy of activation (-7.0 e.u.) is also consistent[10] with an A-1 decomposition. Further support for the assumption that no nucleophile is involved in the rate determining step is found in the large value[11] of k_D/k_H and the nearly equal increase of the rate upon addition of the same molarities of sodium chloride[12] or sodium perchlorate to the reaction mixture. Consequently a unimolecular rate determining step is proposed:

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[6] F.A.Long and M.A.Paul, Chem.Revs. 57, 935 (1957).

[7] E.A.Braude and E.S.Stern, J.Chem.Soc. 1971, 1976, 1982 (1948); J.Koskikallio, Acta Chem.Scand. 14, 1343 (1960).

[8] J.F.Bunnett, J.Amer.Chem.Soc. 83, 4956, 4968, 4973, 4978 (1961).

[9] R.W.Taft, Jr., ibid. 74, 5372 (1952); R.W.Taft, Jr., E.L. Purlee, P.Riesz and C.A.DeFazio, ibid. 77, 1584 (1955).

[10] Bimolecular displacement reaction on a carbon atom adjacent to a sulphonyl group would involve unfavourable steric requirements.

[11] J.G.Pritchard and F.A.Long, ibid. 78, 6008 (1956); ibid. 80, 4162 (1958).

[12] When chloride ions are present $p\text{-}CH_3OC_6H_4SO_2CH_2Cl$ is formed together with II.

$$\underset{\text{III}}{\text{p-}CH_3OC_6H_4SO_2CH_2N_2^{\oplus}} \xrightarrow{\text{slow}} \underset{\text{IV}}{\text{p-}CH_3OC_6H_4SO_2CH_2^{\oplus}} + N_2$$

The carbonium ion IV reacts in subsequent fast steps with a nucleophile to give the products. Favouring a carbonium ion mechanism is also the possibility of stabilisation of IV by mesomeric electron displacements[13] within the $SO_2CH_2^{\oplus}$ group.

The overall conclusion is that α-diazosulphones are behaving similar to the structurally related diazoketones[14] in acid-catalysed hydrolysis, the latter also exhibiting specific hydrogen ion catalysis.

Full details of this work and further investigations on hydrolysis of α-diazosulphones will be published elsewhere.

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13. H.P.Koch and W.E.Moffitt, *Trans.Faraday Soc.* **47**, 7 (1951).
14. C.E.McCauley and C.V.King, *J.Amer.Chem.Soc.* **74**, 6221 (1952); H.Dahn and H.Gold, *Helv.Chim.Acta* **46**, 983 (1963); H.Dahn, A.Donzel, A.Merbach and H.Gold, *ibid*. **46**, 994 (1963).