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A COMPETITION REACTION BETWEEN SUBSTITUTION AND ELECTRON TRANSFER OF 1, 4-DIMETHOXYBENZENES IN CONC. H_2SO_4.[1)]

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It has been reported that 1, 4-dimthoxybenzene (I) in conc. H_2SO_4 gives the corresponding cation radical (II) in a low concentration (0.025%) and that an electron transfer would be preceded by sulfonation of I.[3, 4)]

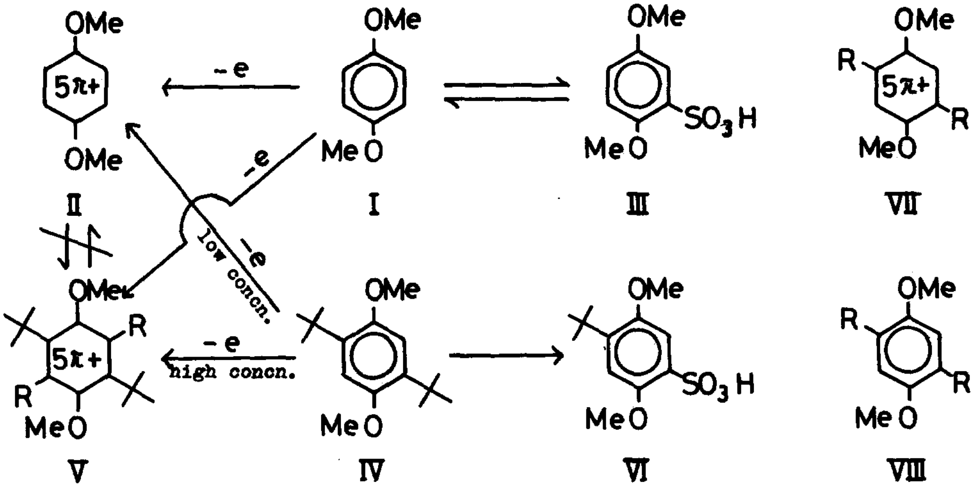
We now found that the solution of I in conc. H_2SO_4 in a few minutes after dissolution at room temperature gave an e. s. r. spectrum corresponding to the radical cation II and yielded 2, 5-dimethoxybenzenesulfonic acid (III) (isolated in 70-90% yield) indicating that the sulfonation took place instantaneously. The acid III when dissolved in conc. H_2SO_4 gave a weak e. s. r. spectrum of the radical II. These facts are easily understood by considering that the equilibrium ($I \rightleftharpoons III$) shown in the scheme is displaced towards III. This prompted us to investigate a competitive reaction between substitution and electron transfer of I in H_2SO_4.

2, 5-Di-t-butyl-1, 4-dimethoxybenzene (IV) dissolved in conc. H_2SO_4 at room temperature gave a brownish yellow solution which in high concentration (5×10^{-3}M) showed an e. s. r. spectrum of nine equidistant lines (1:8:28:56:70:56:28:8:1) with a coupling constant of 2. 87 0e. The spectrum can be rationalized by assuming that the coupling constants of the six methoxy protons and of the two aromatice ring protons happen to be the same in this system. Thus the structure of the cation radical is assigned as V(R = H). This assignment was supported by an e. s. r. study of di-deutero analog V(R = D) which was easily obtained by dissolving IV in D_2SO_4 giving rise to a septet of quintets (a_H = 2. 87 0e. (6H), a_D = 0. 46 0e (2D)). In a 5×10^{-3}M solution of IV in conc. H_2SO_4 the concentration of the radical V(R = H) was about 5 times as high as that of II produced from I. Upon pouring the solution of V(R = H) in H_2SO_4 into ice-water, 4-t-butyl-2, 5-dimethoxybenzenesulfonic acid (VI) was obtained in 60-65% yield. A 10^{-4}M solution of IV in conc. H_2SO_4 showed the e. s. r. spectrum of II. However, when a 10^{-2}M solution of IV in conc. H_2SO_4 giving the spectrum of V(R = H) was diluted with conc. H_2SO_4 to 10^{-4}M, the original nonet of V(R = H) still retained.

These facts indicate that dealkylations of IV takes place only in the neutral molecule while the radical cation is stable against dealkylation. The similar observations were made for alkylation and electron transfer of I. When I was dissolved in conc. H_2SO_4 containing isobutylene, the spectrum of V(R = H) appeared even in low concentrations. On the other hand, when isobutylene was bubbled through a solution of I in conc. H_2SO_4, no spectrum was observed.

Analogous results were obtained, when t-BuOH, propylene or i- PrOH was used instead of iso-butylene. Thus IV dissolved in H_2SO_4 containing i-PrOH or propylene gave the e.s.r. spectrum of VII(R = i-Pr) which was identical with that from 1,4-dimethoxy-2,5-diisopropylbenzene (VIII) (R = i-Pr) in conc. H_2SO_4. On the contrary, VIII(R = i-Pr) in H_2SO_4 containing t-BuOH or isobutylene did not give V(R = H) showing that apparently no alkyl exchange reaction took place. The relative *intensities of the radicals generated from IV, VIII(R = i-Pr) and VIII(R = n-Pr) in conc. H_2SO_4 at concentration of 5×10^{-3}M* were approximately 1, 60, and 60, respectively, showing that concentration of the radicals depends on the susceptibility to dealkylation.

Scheme



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2) Recipient of the Fellowship of Japan Society for the Promotion of Science.

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