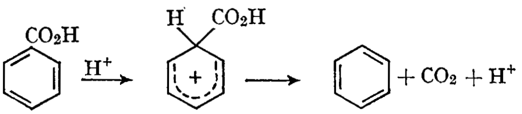
Protodecarboxylation of 2,4-Dimethoxybenzoic Acid

By R. W. HAY and M. J. TAYLOR
(*Chemistry Department, Victoria University of Wellington, Wellington, New Zealand*)

THE possibility of the protodecarboxylation of aromatic acids was first suggested by Schenkel and Schenkel-Rudin[1] in 1948. Experimental evidence for such a reaction has previously been somewhat limited. Schenkel *et al.* gave anthracene-9-carboxylic acid as an example of an acid which is decarboxylated by this mechanism, as kinetic work showed that the decarboxylation occurred more readily in acidic solvents, (sulphuric or dichloroacetic acid) than in basic solvents (7,8-benzoquinoline). Schubert[2] found that the decarboxylation of 2,4,6-trimethylbenzoic acid (mesitoic acid) occurs most readily in sulphuric acid containing *ca.* 1 mole of water per litre, because more concentrated acid yields the acylium ion. The rate of decarboxylation was proportional to the acid concentration.



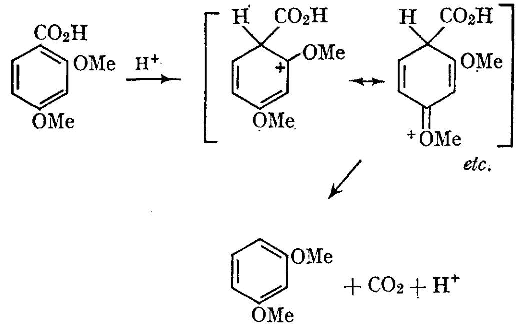
An electrophilic displacement reaction of this type will obviously be favoured by electron-donating substituents in the ring,[3] and we have therefore attempted the decarboxylation of 2,4-dimethoxybenzoic acid in aqueous sulphuric acid solutions. Decarboxylation occurs quite readily even in 2·5M-H_2SO_4 at 60°. The kinetics have been studied manometrically, and also spectrophotometrically at 257 mμ. The decarboxylation is cleanly pseudo-first-order in the carboxylic acid for over 90% of the reaction. The rate of decarboxylation is proportional to the mineral acid concentration (Table) and so provides an excellent example of an S_E2 decarboxylation.[4] The observed dependence of the rate on $[H^+]$ rather than on h_0 indicates[5] that a molecule of water is involved before or during the rate-determining step, which could be interpreted in terms of the reaction:

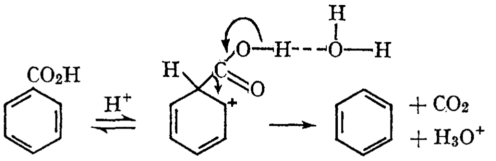
TABLE

Spectrophotometric rate constants at 60·5°

M-H_2SO_4	$10^3 k_{obs}$(min.$^{-1}$)*	$10^3 k_{obs}/[H^+]$ (l. moles^{-1} min.$^{-1}$)
2·514	4·22	1·68
3·75	6·18	1·65
4·99	9·52	1·91
7·66	13·7	1·80
8·00	14·20	1·77

* Mean value of at least two runs





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[1] H. Schenkel and M. Schenkel-Rudin, *Helv. Chim. Acta*, 1948, **31**, 514.

[2] W. M. Schubert, *J. Amer. Chem. Soc.*, 1949, **71**, 2639; see also W. M. Schubert, J. Donohue, and J. D. Gardner, *J. Amer. Chem. Soc.*, 1954, **76**, 9.

[3] R. D. Brown, A. S. Buchanan, and A. A. Humffray, *Austral. J. Chem.*, 1965, **18**, 1507.

[4] B. R. Brown, *Quart. Rev.*, 1951, **5**, 131.

[5] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.