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ACID-CATALYZED CLEAVAGE OF DIMETHYL SULFOXIDE FOLLOWED BY OXIDATION TO METHANESULFONIC ACID

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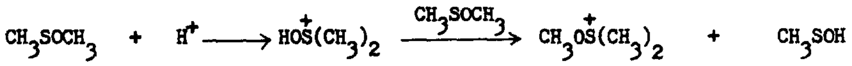
During the study on decarboxylation of tetrahalophthalic acids in dimethyl sulfoxide(DMSO), some inorganic salts were found to have interesting effects(1). We now report a new, novel decomposition reaction of DMSO accompanied by a single and a double decarboxylations of tetrabromophthalic acid.

A mixture of tetrabromophthalic acid(1 mmole), potassium bromide(25 mmoles), and DMSO (25 ml) was stirred and refluxed. Paraformaldehyde sublimed onto the condenser. The solution was yellow at the start of boiling, brown at the 12th minute with evolution of gas, and orange-red at the 18th minute with much gas evolution. The mixture deposited a solid at the 20th minute, and 6 minutes afterwards it exploded. The reaction mixture, therefore, had to be removed from the heater when gas evolution became suddenly violent. The solid(2.1 g, 63% yield based on KBr; mp above 360°) was recrystallized from 95% ethanol. This was found to be potassium methanesulfonate(IR). Anal. Calcd for CH_3SO_3K: C, 8.95; H, 2.25; S, 23.83; O, 35.77; K, 29.14; mol wt, 134. Found: C, 9.05, 9.07; H, 2.13, 2.37; S, 23.76; O, 35.97; K, 29.35; mol wt(cryoscopic in water), 128. NMR spectrum(D_2O): one singlet at δ 2.8. The filtrate was diluted with water and the precipitate(0.30 g) was extracted with benzene. The benzene was chromatographed(alumina and benzene) to get 67 mg(17% yield) of 1,2,3,4-tetrabromobenzene. The residue from the extraction was 2,3,4,5-tetrabromobenzoic acid(0.24 g, 71% yield). Both products were identified by infrared spectra.

The decomposition of DMSO followed by oxidation to methanesulfonate was then found to be catalyzed by acids with pK_a less than 3.1(Table I). Other salts(NaBr, LiCl) also may be used. This reaction may be considered to proceed by protonation to form dimethyl sulfoxonium cation(2), which is attacked by DMSO(3) to give I and methanesulfenic acid(II). Paraformaldehyde is accounted for by decomposition of I(3). II is then oxidized by DMSO(4) to methanesulfonic acid. The role of the inorganic compounds in the decomposition reactions may be to make some reaction step(s) irreversible by salt formation. Sulfenic acid intermediates have been postulated(5) and some stable aromatic sulfenic acids are known(6). The first aliphatic one, t-butylsulfenic acid, has been obtained by thermal decomposition of t-butyl sulfoxide(7).



$$CH_3SOCH_3 + H^+ \longrightarrow HO\overset{+}{S}(CH_3)_2 \xrightarrow{CH_3SOCH_3} \underset{\text{I}}{CH_3O\overset{+}{S}(CH_3)_2} + \underset{\text{II}}{CH_3SOH}$$

$$CH_3SOH + \text{DMSO} \longrightarrow CH_3SO_2H \longrightarrow CH_3SO_3H$$

Table I

Formation of Potassium Methanesulfonate from Dimethyl Sulfoxide(10 ml), Potassium Bromide(10 mmoles), and Acids(1 mmole each)

Acid	pK_a	Reflux Time	Yield, g	% Yield based on KBr
Conc. sulfuric	0.4	6.5 min	1.02	76
Trichloroacetic	0.92	6.5	1.00	75
Phthalic	2.96	11	0.70	52
Fumaric	3.02	25	0.95	71
2-Furoic	3.12	30	0	0
Formic	3.74	30	0	0
Benzoic	4.20	90	0	0

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