The infrared and the NMR data thus provide strong evidence for structure I. The peculiar formation of a substituted dihydro-thiophene ring from a reaction of sulfur trioxide on an alkylated aromatic compound has not previously been reported and an investigation of the mechanism of this reaction and its applicability to other compounds is being continued.

Acknowledgment. The authors are indebted to Professor Dr. H. J. den Hertog (Wageningen) for many helpful discussions and to Professor Dr. Richard H. Wiley (Louisville) for use of the NMR spectrometer.

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Aqueous Mesitoate Electrolysis, Kolbe-Inhibited[1]

Sir:

We wish to report that the aqueous potassium 2,4,6-trimethylbenzoate fails to give typical Kolbe products on electrolysis.[2] This failure will be termed Kolbe inhibition.

Kolbe inhibition is more common in water than in organic solvents and the feature of inhibition in water is the production of oxygen with, sometimes, oxidative degradation. Certain features of structure encourage inhibition such as the presence of a double bond, a cycloalkyl group or an aromatic ring[3] near the carboxyl group.

If the published[4] mechanism is correct then benzenoid inhibition can be explained by an electron deficiency at the carboxyl group. However, Hammett and Treffers[5] showed that when benzoic acid is compared with mesitoic acid as the solute in pure sulfuric acid for freezing point lowering at high dilution, benzoic acid acquires a proton from the solvent to form two particles for every molecule of benzoic acid, while mesitoic acid gives hydroxide ion to the solvent to form four particles for every molecule of mesitoic acid. Presumably, the electron concentration at the carboxylate end of mesitoic acid could be due to the electron donation by *ortho-para* methyls, transmitted by resonance through the benzene ring. Thus, it seems possible that electrons could be withdrawn from the mesitoate ion at the anode to give the Kolbe reaction. Attempted Kolbe electrolysis of potassium mesitoate in water showed that during the course of reaction measurable amounts of carbon dioxide appeared in the anode gas. The electrolyte turned dark with no oil or solid separating, except a minute amount of yellow ether-insoluble material judged polymeric. Absence of other insoluble material negates the formation of any hydrocarbons RR, (R minus H), or mesityl mesitoate, RCOOR. As ROH is a frequent Kolbe product, mesitol was sought in the dark electrolyte. Conventional organic qualitative chemical analysis yielded negative results.

According to Porter and Thurber,[6] mesitol is oxidized by silver oxide to give a quinone free radical of the mesitol, which by proton bonding with a molecule of mesitol gives an analogue of quinhydrone. It is conceivable that the electrolysis of mesitoic acid should yield such a quinhydrone-type organic compound by anodic oxidation if ArOH is present.

Isolation of this compound was attempted without success. Polarographic analysis shows no similarity between the chemically oxidized and the electrolyzed compounds.

We therefore conclude that ring-rupture by anodic oxidation accounts for the carbon dioxide and polymer, and that mesitoic acid is aromatic-inhibited in water. We hypothesize that either carboxylate electron congestion does not occur upon this acid in aqueous solution, or that electron unavailability at the carboxyl is not the cause of benzenoid inhibition. The former idea is supported by the fact that the ionization constant of mesitoic acid is not much lower than that of benzoic acid, both in water at 25°; methyl electron-donation should reduce extent of proton loss. Steric hindrance to carboxyl-and-ring planarity can reasonably account for the lack of electronic transmission, but requires a different explanation for the Hammett[5] results. Perhaps the steric hindrance would tend to push off the hydroxyl group but at the same time prevent the carboxylate ion from getting close to the anode.

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Received March 27, 1961

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[1] Acknowledgment is made to the National Science Foundation, Contract No. G5244.

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