The organic chemistry of the 1,4-cyclohexanedione (CHD)-bromate-sulfuric acid oscillatory system has been revealed by following the reaction of 1,4-CHD with bromate using a GC/MS technique. We could identify 1,4-dihydroxybenzene as an intermediate, 1,4-benzoquinone as the main oxidation, and mono- and dibromocyclohexanedione as the main bromination products. Acid bromate does not cleave the alicyclic ring.

INTRODUCTION

Although uncatalyzed bromate oscillators (UBOs) have been discovered in 1977-8, [1, 2], many systems characterized [3] and a skeleton mechanism proposed two years later [4], our knowledge concerning the organic chemistry of these systems is still rather vague.

The majority of UBOs is composed of an aromatic (mostly a phenol or an aniline derivative), bromate ion and sulfuric acid. The overall reaction is the oxidation and bromination of the aromatic compound. For example, as has been reported earlier.
with phenol as an organic substrate the main products are 1,2-quinone and bromophenols [5].

Under batch configuration most UBOs - after a shorter or longer preoscillatory (induction) period - exhibit only a few, strongly damped oscillations and are highly sensitive to perturbations with halide ions [6, 7].

ALIPHATIC AND ALCYCLIC KETONES AS SUBSTRATES IN BZ-TYPE OSCILLATORS

Now it is widely known that some aliphatic polycarboxylic acids (e.g., malonic, malic, citric) reduce bromate ions in presence of a redox catalyst in an oscillatory manner. More than 20 years ago it has been communicated that the carboxylic acid can be replaced by acetylacetone (2,4-pentanedione) [8]. The only organic product the authors identified was 3-bromo-acetylacetone. What the oxidation products were remained obscure. Later Farage et al. reported that, during the cerium-ion-catalyzed oxidation of cyclomonoketones (cyclopentanone and cyclohexanone) temporal oscillations could be recorded [9]. The authors, however, did not study the chemistry of the reaction.

As regards the chemical transformation of cyclohexanone in a redox reaction the paper by Druliner and Wasserman deserves attention [10]. They reported that the oxidation of cyclohexanone with dioxygen catalyzed by the Co(II)-Br⁻ system resulted in the cleavage of the alicyclic ring. Adipic, glutaric, succinic and capronic acids, and further caprolactone, valerolactone and adipaldehyde were the products of the reaction.

Also the cerium-ion-catalyzed oxidation of 1,3-cyclohexanedione was found to be an oscillatory reaction [11].

A rather unexpected observation was communicated by Farage and Janjic who had found that the 1,4-cyclohexanedione (CHD)-bromate-acid reacting system exhibited oscillatory behavior. Under optimal chemical conditions 200-300 oscillations with period times of a few (2-4) seconds could recorded. They in-