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Martin Izrailevich Kabachnik

Dear Martin Izrailevich,

The Editorial Board of the Journal "Uspekhi Khimii", your coworkers, pupils, and colleagues in joint investigations convey to you their heartfelt greetings on the occasion of your 60th birthday.

As an outstanding chemist, you have been a leading specialist in organophosphorus chemistry in our country. Your remarkable studies on the theory of tautomeric equilibrium and the dual reactivity of tautomeric substances have won you respect among other scientists and your followers both in the Soviet Union and abroad. The new field of complex-forming agents, organophosphorus complexones, which you have created, has opened up wide possibilities for further studies. Your fundamental work

on the reactivity of organophosphorus insecticides with cholinesterase has assisted in the elucidation of the mechanism of their physiological action, which is extremely important for the understanding of a whole series of biochemical processes.

Your amazing capacity for work and keen intellect combined with encyclopaedic knowledge leave us no doubt about further successes of the school which you have established. We value greatly the opportunity of working with you.

We wish you health and new creative successes in your scientific and public activities.

Editorial Board of "Uspekhi Khimii"

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Oxidation of Benzene

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The review gives a systematic account of studies on the oxidation of benzene by different methods—with oxygen in the gas phase, with Fenton's reagent in aqueous solution, under the action of light and penetrating radiation, and also catalytic oxidation in aqueous solution. Particular attention has been paid to the mechanism of the oxidation of benzene; the main experimental evidence for individual mechanisms is discussed and unlikely schemes are criticised. Kinetic data and the mechanism of the catalytic oxidation of benzene to phenol with oxygen in aqueous solution in the presence of iron and copper ions which follows from them are discussed in detail. The bibliography incorporates 120 references.

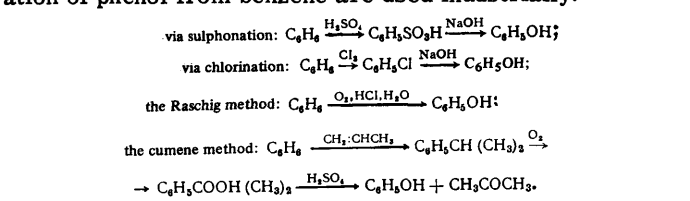
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I. INTRODUCTION

Benzene differs sharply from other hydrocarbons by its high stability with respect to oxidation, which is due to its structure. Hydrocarbons are known to be oxidised by a free-radical mechanism, the reaction including a stage involving the homolytic abstraction of a hydrogen atom. The high stability of the C–H bond in benzene (102 kcal mole^{-1}) is one of the reasons for its stability. No less important is another factor, namely the major role played in the oxidation of hydrocarbons by hydroperoxides, which break down into free radicals and initiate further chain oxidation. The corresponding hydroperoxide is not known for benzene and attempts to synthesise it have proved unsuccessful, and it appears that it does not exist as a stable molecular compound. The absence of a hydroperoxide as the species initiating the reaction does not favour rapid oxidation. Finally, it is very significant that the oxidation of benzene yields phenol and products of its further oxidation, which behave as inhibitors of chain reactions involving the oxidation of hydrocarbons. All these factors explain the stability of benzene with respect to oxidation.

The oxidation of benzene to phenol is of practical importance. Nowadays the following methods for the preparation of phenol from benzene are used industrially:



These procedures, including the cumene method which is the most economical, consist of many stages. Therefore the development of an effective single-stage process is important. As will be seen from the present review, under certain conditions it is possible to oxidise benzene to phenol with a fairly high yield. The theoretical possibility of oxidising benzene to phenol under mild conditions is a consequence of the existence of enzymes which can, for example, oxidise phenylalanine to tyrosine.

II. GAS-PHASE OXIDATION OF BENZENE

The first studies on the oxidation of benzene with molecular oxygen in the gas phase were performed in the 1920's. The gas-phase oxidation of benzene takes place at 500–700°C.[1-31] The oxidation yields phenol, resins, carbon monoxide, and carbon dioxide. At these high temperatures the oxidation of benzene is accompanied by its cracking on the wall of the reaction vessel. Glass packing favours the cracking process[27]. As a result of cracking, low-molecular hydrocarbons (methane, ethylene, acetylene, etc.) are formed together with the oxidation products[19,20,27]. In a number of investigations homogeneous catalysts, such as hydrogen chloride, nitrogen dioxide, and iodine were used. As an example, one may quote the experiments with iodine in which the introduction of 0.02% of iodine into air at 604°C increased the yield of phenol from 40.4% (without iodine) to 56.5% with respect to unreacted benzene[12]. In order to accelerate the oxidation of benzene, atomic oxygen obtained in an electric discharge has also been used[13,21,22]. The oxidation of benzene has been stimulated by readily