Radiation-induced dimerisation of benzene in the presence of anionic nucleophiles

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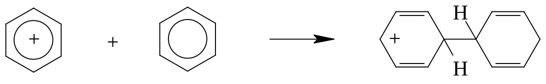
The logarithm of the rate of radiation-chemical dimerisation of benzene appears to be a linear function of the enthalpy of ionisation of anionic nucleophiles solubilised with crown ethers.

Oligophenyls, better known as polyphenylenes, possess a unique combination of chemical resistance, mechanical strength and electrophysical properties which make them quite promising materials for practical application in electrical engineering and electronics.[1–5] Poly(*p*-phenylene) contains 6 to 15 repeating units in its molecule, depending on the preparation procedure. The most popular procedures for preparing poly(*p*-phenylene) are chemical (oxidative) and electrochemical (anodic) polymerisations of benzene or biphenyl. It has been noted[3] that radiolysis of benzene has much in common with its oxidative polymerisation. The radiation polymerisation of benzene is not superior to conventional procedures but does offer advantages for studying the polymerisation mechanism since it is not complicated by electrode reactions or side processes with the participation of chemical agents involved in the process.

The primary step in all of these polymerisation processes is the formation of benzene radical cations by one-electron oxidation. The radical cation further results in formation of polyphenylene *via* electrophilic attack on the benzene molecule or by a so-called ‘stair-step’ mechanism. It is impossible to choose between these two mechanisms. In the former case, the arenium ion is formed as an intermediate, reaction (1).



(1)

When a nucleophile is present, either intentionally or unintentionally, this intermediate eliminates a proton as the leaving group to give a radical which can disproportionate to biphenyl and phenylcyclohexadiene or is reduced to partially hydrogenated biphenyl. The radical cation can also react with a high probability with nucleophilic agents which are either oxidised to give a benzene molecule or added to the benzene ring. The likely reactions of nucleophilic agents with aromatic radical cations were detailed by Yoshida.[6] Ionising radiation produces radical cations in a low concentration unless a very high dose rate is employed; therefore, the dimerisation of benzene radical cations to dications can be ignored.

In this work we focus our attention on the formation of the end product, the oligomer, by γ-radiolysis of benzene in the presence of anionic nucleophiles, which are likely to reduce the radical cations, thus preventing polymerisation. The conventional scheme of cationic polymerisation of benzene by electrophilic attack suggests the stepwise formation of the oligomer through stable products, *i.e.* benzene → biphenyl → *p*-terphenyl → *p*-quaterphenyl → *etc.*, rather than chain propagation involving radical cations. In order to obtain quantitative results, we consider it reasonable to restrict ourselves to the stage of formation of the dimeric compounds since the determination of biphenyl and its hydrogenated derivatives is easy and reliable. We employed rather low doses of γ-radiation at which these dimers prevail in the product.

Inorganic anions cannot be obtained in benzene solutions unless special measures are taken. In this work we solubilised the inorganic compounds KOH, KBr, KI, $K_2C_2O_4$ and $KMnO_4$ by means of 18-membered crown ethers. Solutions of benzene and naphthalene radical anions were also prepared. These radical anions were generated by dissolving potassium metal in benzene containing 18-crown-6 under high vacuum. There are some speculations on the nature of the counterion when potassium is solubilised by a macrocyclic compound in benzene. Three types of species may be anticipated, *viz.*, the potassium anion K^-, the solvated electron e_{solv} and the radical anion $C_6H_6^{-\cdot}$. Although they can transform into one another and are likely in equilibrium, we prefer the latter in order to be consistent. Unfortunately, we were unable to obtain convincing evidence for the existence of the benzene radical anion in this system at room temperature by spectrophotometric measurements, unlike the case of naphthalene in which a well-resolved absorption spectrum of the naphthalenide ion allowed even quantitative measurements. 18-Crown-6, dicyclohexano-18-crown-6 and di-*tert*-butyldibenzo-18-crown-6 were used as the solubilising agents at a concentration up to 0.1 mol dm^{-3}. Concentrations of nucleophile species in the initial solutions were in the range 4×10^{-3}–1.4×10^{-2} mol dm^{-3} as determined by atomic emission spectroscopy or ion chromatography. Preliminary experiments showed that an increase in crown ether concentration starting from 0.05 mol dm^{-3} exerted no effect on the rate of radiation-induced dimerisation of benzene in the presence of a particular nucleophile, although it did affect the solubility of inorganics. There was also little difference between unsubstituted and substituted 18-crown-6 ethers, but the ring size did affect the results. All of the solutions were prepared in reagent grade benzene, additionally purified and thoroughly dried. Before irradiation, samples were outgassed by a freeze–pump–thaw technique and sealed in glass ampoules.

Irradiations were performed on a ^{60}Co γ-source at room temperature and a dose rate of 4 Gy s^{-1} to doses that did not exceed 35–40 kGy. Biphenyl, phenylcyclohexa-2,4-diene and phenylcyclohexa-2,5-diene were determined by gas–liquid chromatography. To be sure that they were the majority products, the proportion of higher molecular weight compounds was monitored by microcolumn high-performance liquid chromatography or gravimetry.[7] No products such as phenol or bromobenzene (in the case of KOH or KBr, respectively) that could be associated with the nucleophilic addition to the radical cation were detected by gas chromatography and spectrophotometry. It is well known that the radiation-chemical yield of reaction G is proportional to the rate of the reaction. Thus, the rate of benzene dimerisation was measured as the radiation-chemical yield of consumption of parent molecules $G(-C_6H_6)$, molecule/100 eV, *i.e.*, the doubled yield of dimeric products determined by chromatography.

The rate of electrochemical (anodic) polymerisation of aromatic compounds is known to increase with the oxidation potential.[5,6] The oxidation potential of a compound in the liquid phase can be correlated with the Gibbs energy of ionisation in the gas phase or, knowing that the entropy of ionisation is low, with the gas-phase ionisation energy (enthalpy). In this work we have examined only one monomer (benzene) with various nucleophilic additives and found that the rate of dimerisation correlates with the gas-phase enthalpy of ionisation of the additive (Figure 1). These enthalpies were calculated from the relevant standard enthalpies of formation[8] or taken as measured or calculated values of the electron affinity of the corresponding neutral species.[9–11] It can be seen from Figure 1, that the logarithm of the rate (radiation-chemical yield) of dimerisation of benzene is a linear function of the enthalpy of ionisation of a nucleophile (the coefficient of correlation is 0.970). For the oxalate ion, we consider the ionisation enthalpy the same as the experimental electron affinity of carbon dioxide (–0.40 eV),[12] which is a reasonable approximation; nonetheless, the rate of dimerisation in the presence of potassium oxalate is given just as an illustration. Note that if this value is true for oxalate, the correlation coefficient will be 0.973 instead of 0.970.

This correlation is consistent with the conventional mechanism of cationic polymerisation of benzene (by electrophilic attack), but we believe that these nucleophiles reduce the primary radical cation rather than abstract a proton from the arenium ion. Otherwise, we would have a correlation with the proton affinity of the nucleophiles, which is not the case.

Thus, the results obtained may also be of some help in performing electrooxidative polymerisation of aromatics. Ions comprising the supporting electrolyte are to be selected among those that possess a higher enthalpy of ionisation, thus providing a maximum rate of polymerisation.

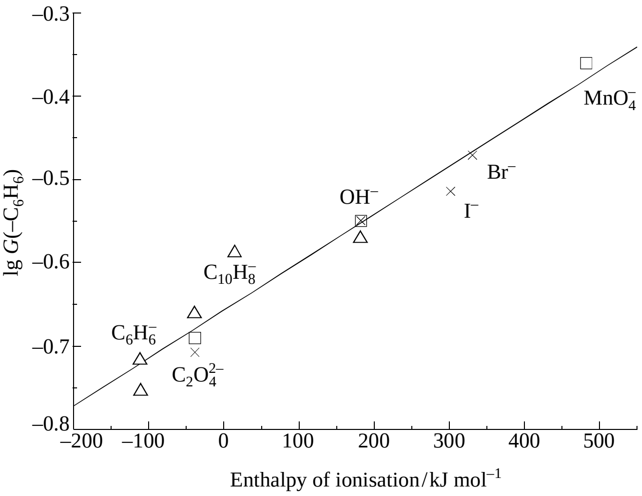


Figure 1 Semilogarithmic plot of the rate of radiation-induced dimerisation of benzene as a function of the enthalpy of ionisation of anionic nucleophiles in the gas phase: $G(-C_6H_6)$ is the radiation-chemical yield of consumption of the monomer; △, × and □ refer to 18-crown-6, dicyclohexano-18-crown-6 and di-*tert*-butyldibenzo-18-crown-6 as solubilising agents, respectively.

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Received: Moscow, 19th May 1997
Cambridge, 15th July 1997; Com. 7/03541A