REACTIONS OF LOW PRESSURE OXYGEN PLASMAS WITH LIQUID AROMATIC COMPOUNDS

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ABSTRACT

The oxidation of twelve aromatic compounds with either high voltage or radio frequency glow discharges has been studied. The reactions have been carried out by making the oxygen plasma reach the low vapour pressure substrate. The results obtained in the plasma-liquid interactions of this work considerably differ from those in homogeneous gas phase. Neither fragmentation products in the traps nor polymers on the reactor walls have been detected. Products formation has proved to be more selective as well. Total conversion, i.e., mass transformed against initial mass of substrate, has been studied as a function of temperature of the liquid and oxygen flow rate in the reactor, this ranging from 10 to 20 mMol/h. The optimum conversions were 7 to 40%. A correlation between these results and the behaviour of the $O(^3P)$ population in the discharge has been arrived at.

1. INTRODUCTION

Reactions of oxygen atoms with organic molecules have been reported by a number of investigators. Most published works have been devoted to olefins and aromatic hydrocarbons in the gas phase [1-12], but only a limited number to reactions in the condensed phases [13-17], including some alkanes. We wish to make a report on work with ground-state atomic oxygen, $O(^3P)$, and aromatic compounds in the liquid phase.

The first studies of oxygen atoms addition to hydrocarbons in condensed phases were performed with olefins [13-15]. In either case they have concentrated on the discussions about the pathways for the reactions. Based upon products distribution for diverse starting compounds, the intermediacy of triplet diradicals has been proposed by some authors [13,14] while others have formulated an "epoxide-like" transition complex [15]. To our knowledge there is only a preliminary report on the oxidation of condensed aromatic compounds [20]. With the aim of giving a more complete description of these reactions and comparing the results with those obtained in the gas phase with the same compounds [12], more species have been selected for studying the O atom addition to them.

2. EXPERIMENTAL

The reactions were carried out by making an oxygen cold plasma reach the low vapour pressure liquid substrate. Two experimental set-ups were employed: a high voltage discharge and a radio frequency device [20]. In both cases the reactor was a double walled glass vessel of c.a. 300 ml. In the high voltage system it was supplied with two electrodes made of aluminum and Teflon. Oxygen was introduced into the reactor through one of the electrodes, which was hollow. The plasma was produced by means of a home-made low frequency high voltage AC power source that supplied up to 7 kV and 200 mA. The optimum distance between the electrodes and the liquid surface for maximum conversion was found to be 33 cm.

In the radio frequency system the plasma was produced by means of a Branson IPC 100 generator with a fixed frequency of 13.4 MHz and variable power up to 500 watts. In order to obtain an efficient coupling of the source to the discharge, a matching box was utilized to connect the generator to the rf coil. This was placed around the reactor approximately 16 cm away from the bottom.

Substrate (1.5 to 3 ml) was placed at the bottom of the reactor and this was cooled down by means of a methanol-liquid nitrogen bath, the temperature being controlled within ±1°. The liquid was magnetically stirred and the system was connected to a vacuum line equipped with two traps used to collect any possible volatile product and to protect the mechanical vacuum pump. The oxygen flow was measured with a 247 B-MKS flow meter and the pressure was monitored with a thermotron TM111 Leybold-Heraeus. In order to study the $O(^3P)$ population, the light from the discharge was focused onto the entrance slit of a 2.0 m Jarrell-Ash Czerny-Turner scanning spectrometer equipped with a 1808 lines/mm grating. The emission signal was detected by an RCA 4832 photomultiplier that fed a lock-in amplifier, and was finally recorded on a Cole-Parmer pen recorder.

Products of the reactions were identified by means of GC-MS. A HP 5995 apparatus that utilizes a HP 2671G processor was used. The gas chromatograph was equipped with a 25 m fused silica capillary column. Aldrich p.a. products were used as standards.

3. RESULTS AND DISCUSSION

Twelve aromatic compounds have been oxidized by using reaction systems activated with either high voltage or radio frequency discharges. For each substrate, volume, applied power and time of reaction have been maintained constant. The latter was rather short (30-60 min.) in order to obtain not a high oxidation and hence to have minimum successive reactions.

3.1 Anisole

The oxidation of anisole was carried out by using a high voltage oxygen plasma. Applied power was 24.3 W and time of reaction was 30 minutes for 2 ml of substrate. The total percentage of conversion, i.e., mass transformed against initial mass of methoxy phenol, has been plotted in Fig. 1 as a function of oxygen flow rate at -50°C. The shape of the curve is very similar to those reported for n-hexane and n-heptane [17]. Oxygen presssure at what maximum conversion was achieved is c.a. 0.29 torr.

The behaviour of anisole conversion rate against temperature of the liquid is presented in Fig. 2. Oxygen flow was fixed at the optimum value of 26.8 mMol/h ($p(O_2)\cong 0.29$ torr). The vapour pressure of anisole at its freezing point (-37.5°C) is 0.034 torr, calculated by extrapolation of reported values ($\log_{10}p$ versus $1/T$). This value is too high to guarantee that competing gas-phase reactions do not take place. Due to this fact 1:1 mixtures of anisole and t-butylbenzene were prepared prior to treatment with the oxygen plasma. Because of its relative inertness (see Table I), t-butylbenzene can serve as solvent for the plasma oxidation. The use of solvents in plasma reactions has been preliminarily tested [21]. It seems to be restricted to compounds that have a lower or similar vapour pressure as the substance to be oxidized. If it is higher, no reaction with the substrate occurs; it seems to be likely that the vapour of the solvent prevents attacking species from reaching the liquid surface.

The maximum anisole conversion was achieved at c.a. -57°C. Again the situation is very similar to those reported for toluene [20], n-hexane and n-heptane [17], the reactivity decreasing when the temperature is either lower or higher than the optimum range. At this point the calculated vapour pressure of the anisole solution is 3.6x10^{-3} torr. This gives a ratio p(O_2)/(vapour pressure of the mixture)≅82.

The main products have been identified as ortho-, meta- and para-methoxyphenols, which amount to 86% of the total yield. The total byproducts are a mixture of the six dihydroxy-methoxy-benzenes obtained from the attack of oxygen atoms to methoxy phenols.

3.2 Ethylbenzene

Ethylbenzene was also oxidized by means of a high voltage oxygen plasma. Applied power was 22.4 W and time of reaction was 1 hour for 1.5 ml of substrate. The maximum ethylbenzene reactivity (13.2% conversion) was observed at about 24.1 mMol/h of oxygen (p(O_2)≅0.27 torr). The extrapolated vapour pressure of ethylbenzene at -90°C is 3.14x10^{-4} torr. This gives a ratio p(O_2)/p(ethylbenzene)≅86. The three ethylphenols made up 84% of the products. The remainder consisted of 1-phenylethanol (7%), acetophenone (5%) and dihydroxy-ethylbenzenes (4%).

3.2 Experiments with the other compounds

For the rest of the compounds, the results are very similar. The case of m-xylene is very interesting. Its freezing point is -47.9°C, hence a 13.6% v/v solution was prepared with iso-octane as solvent. The mixture was studied, by using the radio frequency system, at temperatures ranging from -100 to -60°C. The results were plotted in Fig. 4 where it is observed that the maximum conversion (20.8%) was reached at -90°C (vapour pressure of the solution≅4.2x10^{-3} torr) and it practically kept constant as the temperature was lowered even to -105°C. At this point, the mixture was about to start solidifying. The main products were 2,6-dimethylphenol and 2,4-dimethylphenol. They amounted 94% of the total yield. As t-butylbenzene did with m-anisole, iso-octane proved to be a good solvent, its conversion being only 4%.

The other monoalkylbenzenes followed the same pattern as ethylbenzene, the conversion being lower as the alkyl group was more bulky. With the di- and tri-alkyl derivatives the reactions were more selective. 1,3,5-Trimethylbenzene, for instance, gave 91% of 2,4,6-trimethylphenol.

The results obtained in the plasma-liquid interactions of this work differ considerably from those in homogeneous gas phase [12,22-24].

Primary results for toluene [20] have been shown to be very much similar to the observations of this study. A maximum conversion of 10.6% was observed at -95 °C and oxygen pressure of 0.09 torr, this being 105 times higher than the vapour pressure of toluene. The main products were o-, p- and m-cresols (70%, 15% and 8%, respectively).

For the rest of the compounds, $p(O_2)$/(vapour pressure) is in the range 10-120, thus confirming the importance of this ratio when getting optimum reactivity of $O(^3P)$ with these compounds. At low oxygen pressures the production of $O(^3P)$ in the plasma through the process

$$O_2 + e^- \rightarrow O + O + e^- \qquad (1)$$

decreases for there are less oxygen molecules that can suffer electronic impact (O may be ^3P, ^1D, ^1S, etc.). At the side of higher pressures, due to higher concentration of O_2 in the plasma, the frequency of collisions between these species and the electrons increases. This implies that the electrons do not have time to be sufficiently accelerated by the electric field and hence most of them do not acquire high enough energy to produce the dissociation of O_2, thus generating less $O(^3P)$ atoms. The region of optimum oxygen pressure is obviously a compromise between the two tendencies. This behaviour was demonstrated by following the relative population of O I (2p ^3P). This can be correlated to the 3p $^3P \rightarrow$3s ^3S (λ=844.6 and 844.7 nm) transition. The glass reactor was modified by fitting a window to it in order to focus the light from the discharge into the entrance slit of the Jarrell-Ash spectrometer. The signal of O I was recorded and plotted versus the oxygen pressure in the reactor [17]. The whole vacuum system had to be simplified in order to place the reactor in front of the spectrometer. This is perhaps the reason why the region of optimum oxygen pressure does not exactly match that necessary for the maximum conversion of the compounds but the behaviours of conversion vs. O_2 flow rate are very similar to that of the oxygen signal. The explanation for the behaviour of the reactivity versus temperature has been given elsewhere [17].

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