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The Effect of O_2 and NO_2 on the Ring Retaining Products of the Reaction of Benzene with Hydroxyl Radicals

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Summary. The reaction of benzene with hydroxyl radicals affords phenol and 1,4-benzoquinone in 0.18 ± 0.05 and 0.02 ± 0.01 yield, respectively. The main reaction of the hydroxycyclohexadienyl radical with oxygen leads to the respective peroxy radical which in turn decomposes to ring cleavage products and phenol. In the presence of NO_2, nitrobenzene is also formed with yields depending linearly on the initial NO_2 concentration and vanishing as $[NO_2]$ approaches zero. The amount of phenol formed in the presence of NO_2 is equal to that formed in the absence of NO_2 within experimental error.

Keywords. Phenol; 1,4-Benzoquinone; Nitrobenzene; Benzene; Hydroxyl radical.

Der Einfluß von O_2 und NO_2 auf die cyclischen Produkte der Reaktion von Benzol mit Hydroxylradikalen

Zusammenfassung. Die Reaktion von Benzol mit Hydroxylradikalen liefert Phenol und 1,4-Benzochinon in Ausbeuten von 0.18 ± 0.05 und 0.02 ± 0.01. Die Hauptreaktion des Hydroxycyclohexadienylradikals mit Sauerstoff führt zum entsprechenden Peroxyradikal, das seinerseits zu offenkettigen Produkten und Phenol zerfällt. In Gegenwart von NO_2 entsteht Nitrobenzol; seine Ausbeute hängt linear von der Anfangskonzentration an NO_2 ab und läßt sich für verschwindende NO_2-Konzentrationen nach Null extrapolieren. Die Menge an gebildetem Phenol hängt nicht von der An- oder Abwesenheit von NO_2 ab.

Introduction

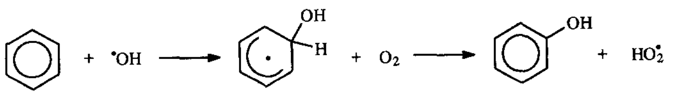
It is well established that the main degradation route of aromatic hydrocarbons in the atmosphere proceeds *via* reaction with hydroxyl radicals. Alkyl substituted aromatic hydrocarbons react to more than 90% by addition of an OH radical to the aromatic ring and to less than 10% by hydrogen abstraction from the alkyl substituent [1].

In the case of benzene, the OH radicals add exclusively to the aromatic ring with hydrogen abstraction being negligible. In the first study of this reaction in the presence of NO_x by *Hoshino et al.* [2], phenol and nitrobenzene were reported to be the products formed through the reaction of the OH-benzene adduct (hydroxycyclohexadienyl radical, henceforth called "adduct") with O_2 and NO_2. Following the above study, the ring opening products formaldehyde, formic acid, and maleic anhydride were reported to account for 15–20% of the reacted carbon [3]. The first yields of phenol and nitrobenzene were reported by *Atkinson et al.* [4] phenol, 0.236, nitrobenzene $0.0336 + 3.07 \times 10^{-16}$ $[NO_2]$ (NO_2 in molecular units) and by *Evmorfopoulou* and *Glavas* [5] (phenol, 0.10). In Ref. [4], however, the nitrobenzene yield did not extrapolate to zero when no NO_2 was added, and the authors concluded that the OH-benzene adduct reacted only with NO_2 and not with O_2. The resuls of *Knispel et al.* [6] have shown that under atmospheric conditions the OH-benzene adduct reacts predominantly with molecular oxygen and not with NO_2 (at $[NO_2] \leqslant 1.6$ ppm(v/v), 4×10^{13} molecules/cm^3). The reaction of the adduct with nitrogen monoxide is less pronounced. This apparent disagreement was solved by *Atkinson* and *Aschmann* [7] by reevaluating their results discussed in Ref. [4], accepting that the formation of nitroaromatics occurs *via* competitive reactions of the adduct with O_2 and NO_2.

In the present work, we have studied the formation of the products in air and in a nitrogen atmosphere. We report for the first time the yields of phenol and 1,4-benzoquinone under NO_x-free conditions. In addition, we report the yields of the observed products in the presence of NO_x and compare them with the existing ones in the literature [4, 5]. We have also examined the effect of changing the initial concentration of oxygen and nitrogen dioxide on the formed products and can thus confirm or negate reactions of the adduct with these two reactants proposed in past studies.

Results and Discussion

The major ring retaining products observed were phenol, 1,4-benzoquinone, and – in the presence of NO_2 – nitrobenzene and traces of *o*-nitrophenol. The yields of these products, reported as weight of formed product *vs.* weight of consumed benzene, varied depending on the employed reaction conditions. In the absence of NO_x and in experiments carried out in an air matrix, phenol and 1,4-benzoquinone were the sole ring retaining products identified in the gas phase. As shown in Fig. 1, increasing the oxygen concentration by a factor of 15 resulted in an increase of phenol formation of approximately 20%. The amounts of phenol at high and low oxygen concentration are statistically different at the 0.2 confidence level. In the case of 1,4 benzoquinone, the amount formed in an air matrix was 40% of the amount formed in a nitrogen matrix; this difference is statistically significant at the 0.001 confidence level. When, however, the yields are calculated, the differences in the yield of both phenol and 1,4 benzoquinone at low and high oxygen concentration become statistically insignificant because of the large variation in benzene consumptions. Given these uncertainities, the obtained yields were 0.113 ± 0.052 and 0.073 ± 0.022 for phenol and 0.017 ± 0.010 and 0.025 ± 0.014 for 1,4-benzoquinone at high and low oxygen concentrations, respectively. A simple reaction scheme compatible with the observed data could be the following:



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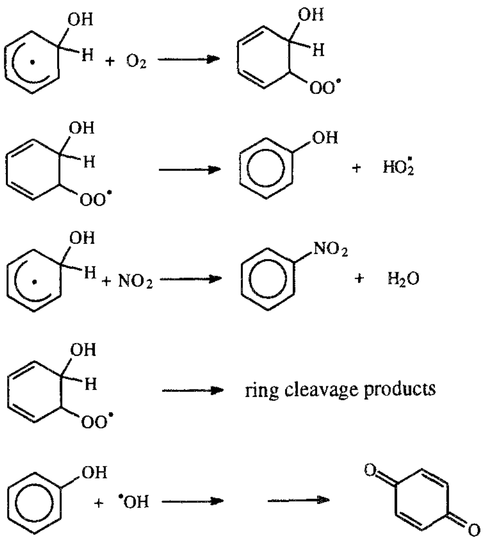

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The observed results show that reaction 4 is the main route of the reaction of the adduct with oxygen. This interpretation is in contrast to the results of *Bandow et al.* [3] who proposed that the ring cleavage products could not account for more than 15–20% of the reacted carbon, but it is in agreement with other recent studies [8, 9] which reported on ring retaining and cleavage products and obtained low mass balances (in the order of 50% of reacted carbon) for the analogous system of toluene. An explanation of the low mass balance, in addition to the postulation of the existence of here unidentified ring cleavage products, is the formation of condensed phase products which accumulated on the teflon walls of our chamber after repeated experiments. For this reason, a new teflon bag was used after every six experiments.

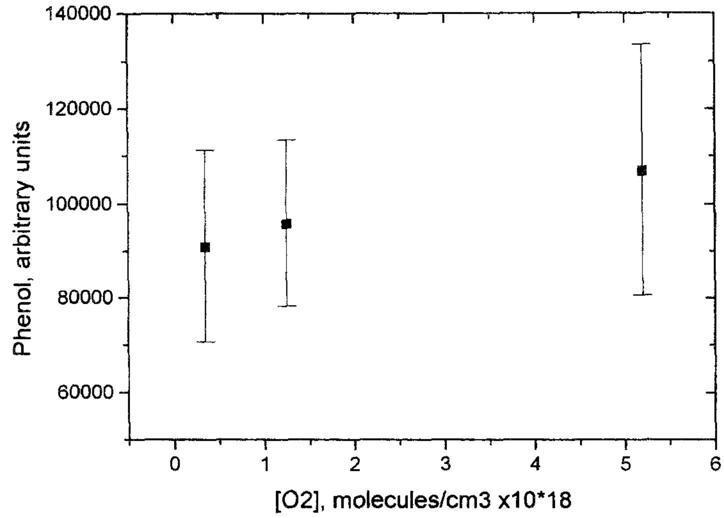

Fig. 1. Plot of the amount of formed phenol (arbitrary units) *vs.* oxygen concentration in absence of NO_2; error bars: one standard deviation

The actual mechanism of the formation of phenol from the reaction of the adduct with oxygen is practically unknown. The two already existing fast kinetic studies contradict each another. In the first one [10], indirect evidence was provided for the occurrence of reaction 1 through the measurement of the regenerated hydroxyl radicals after reaction of the formed hydroperoxy radicals with added NO. In contrast to these results, *Bjergbakke* and *Pagsberg* [11] reported that reaction 1 is of minor importance, the main reaction being 2; and phenol is formed *via* benzene + OH → phenol + H (7). In order to contribute to this question, computer simulations were carried out with the FACSIMILE software. A simple reaction scheme was used in which the rate constants of the adduct with oxygen and NO_2 reported by *Knispel et al.* [6] were employed. The photolysis rate constant of hydrogen peroxide was adjusted so that the simulated decay profile of benzene would fit best the experimentally observed profile. If only reaction 1 were employed in this reaction scheme, the simulation produced six times as much phenol as experimentally determined. When, however, reactions 2, 3, and 4 were introduced with reactions 3 and 4 weighted by the factors 0.07 and 0.93 and reaction 1 amounting to 20% of reaction 2, the yields of phenol and 1,4 benzoquinone fitted best the experimental results. In separate experiments, phenol reacted with H_2O_2 under our UV irradiation, and 1,4 benzoquinone was identified to be the major product with a yield of 25 ± 10% of reacted phenol. This result explains the yield of benzoquinone (0.02) observed in the benzene experiments where the phenol yield was about 0.1.

The rate constants of the reaction of the adduct with O_2 and NO_2 as reported by *Zetzsch* and coworkers [6] are 1.9×10^{-16} and 2.5×10^{-11} cm^3/s, respectively. In order to examine the effect of added NO_2 on the formed products, these experiments were carried out in a nitrogen matrix. Therefore the oxygen content would be low and thus the adduct would react predominantly with NO_2. As shown in Fig. 2, increasing $[NO_2]_0$ by a factor of ten had no effect on the amount of formed phenol, in agreement with *Atkinson et al.* [4]. On the basis of this result, the reaction

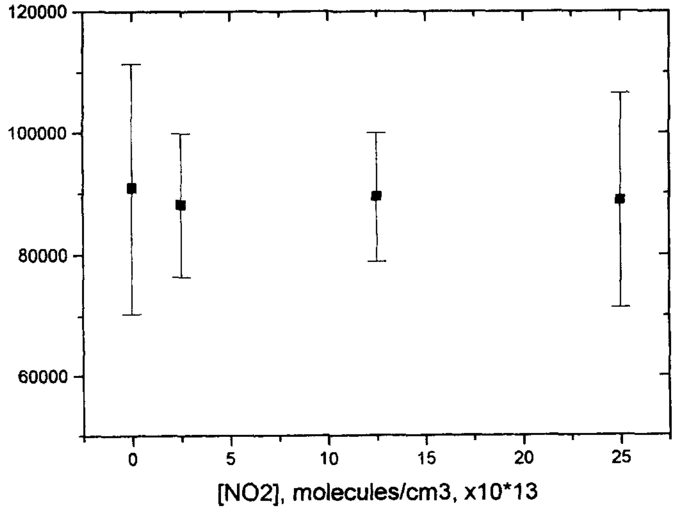

Fig. 2. Plot of the amount of formed phenol (arbitrary units) *vs.* initially added NO_2 concentration at low oxygen concentration; error bars: one standard deviation

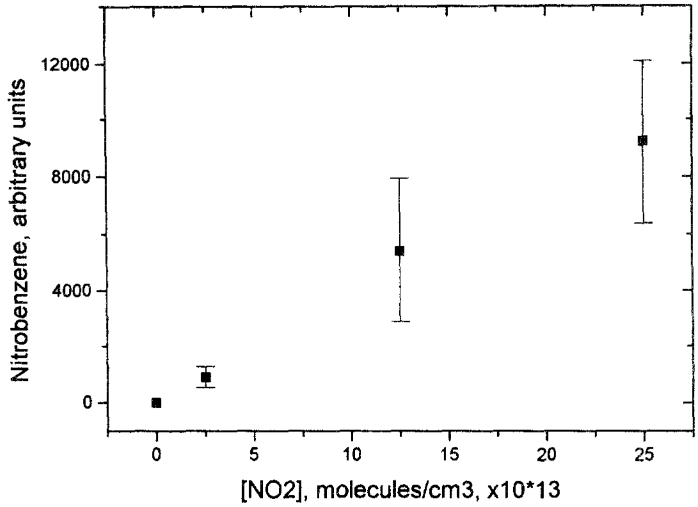

Fig. 3. Plot of the amount of formed nitrobenzene (arbitrary units) *vs.* initially added NO_2 concentration at low oxygen concentration; error bars: one standard deviation

proposed in Ref. [7] (adduct + $NO_2 \rightarrow$ phenol + HONO, 8) is shown to produce similar phenol yields as reactions 1 and 3. *Bjergbakke* and *Pagsberg* [11] also did not observe increased phenol formation when increasing $[NO_2]_0$. At the same time, however, these authors did not report the formation of nitrobenzene either. The amount of formed nitrobenzene, shown in Fig. 3, increased linearly with increasing the initially added NO_2, consistently with reaction 4. It must be pointed out that the amount of formed nitrobenzene extrapolates to zero as $[NO_2]_0$ approaches zero, in contrast to the results of *Atkinson et al.* [4] who observed a non-zero intercept. It is not meaningful to compare the yields of nitrobenzene reported here with those of Refs. [4, 5] becasue the yield depends strongly on the concentration of NO_2 and also on the ratio of $[NO_2]_0$ to [benzene]. Thus, in Fig. 3 $[NO_2]$ means the initially added amount of NO_2, whereas in Ref. [4] the NO_2 concentration is the calculated value at the time of the measurement of nitrobenzene. In Ref. [5], the initial NO_2 concentration was approximately an order of magnitude larger than the one employed here. Simultaneously, in Refs. [4, 5] the initial benzene concentration was 0.05 to 0.5 of the NO_x (NO + NO_2) value. The amount of formed nitrobenzene at $[NO_2]_0 = 2.5$ and 12.5×10^{13} molecules/cm^3 are significantly different at the confidence level 0.0001, whereas the nitrobenzene values at $[NO_2]_0 = 12.5$ and 25×10^{13} molecules/cm^3 are different at a confidence level of 0.05. In contrast, the nitrobenzene yields of 0.0006 ± 0.0003, 0.004 ± 0.002, and 0.006 ± 0.004 at $[NO_2]_0$ values of 2.5, 12.5, and 25×10^{13} molecules/cm^3, respectively, were not significantly different because of the large variation in the measurement of consumed benzene as was the case for phenol. In addition to the experiments carried out in a nitrogen matrix, ten experiments were carried out with an initial NO_2 concentration of 2.5×10^{14} molecules/cm^3 in an air matrix. In these experiments, the phenol yield was 0.09 ± 0.03, in good agreement with the value of 0.10 obtained in our past study [5]. Phenol, however, reacts 21 times faster than benzene with OH radicals. For the consumption of benzene in our experiments (6%), the correction factor of phenol is calculated to be 1.8. Thus, the phenol yield increases to 0.16 and 0.20 in the presence and absence of NO_2, respectively, close to the yield (also corrected for the OH reaction) reported in Ref. [4] (0.24). In these experiments, the nitrobenzene yield was approximately 65% of the value reported for the nitrogen matrix experiments. However, this difference was not statistically significant. Traces of *o*-nitrophenol were also observed at the highest employed NO_2 concentration. Presumably, *o*-nitrophenol is a secondary product either of phenol or nitrobenzene.

It is apparent from the above discussion that significantly more work needs to be done on these systems, particularly as the aromatic hydrocarbon fraction in the nonmethane hydrocarbons of the urban centers increases with increasing use of cars equipped with catalysts.

Experimental

All experiments were carried out in FEP Teflon chambers of volume 400 l. The chambers were housed in an aluminum box thermostatted at 25 ± 2 °C. An NO_x free source of hydroxyl radicals was provided by the photolysis of H_2O_2 vapours by Philips UV lamps. Two series of experiments were carried out. In the first one, the experiments were performed in air obtained from an Aadco pure air generator; in the second series, the experiments were conducted in nitrogen of 99.999% purity. Although every precaution was taken to keep the oxygen content in the chabers filled with nitrogen as low as possible, the oxygen concentration in the chamber measured with an electron capture detector was around 3.5×10^{17} molecules/cm^3, 6.66% of the ambient air oxygen content. The initial benzene concentration was 1.3×10^{16} molecules/cm^3 and that of hydrogen peroxide 2.5×10^{16} molecules/cm^3 for all experiments. This benzene concentration was selected in order to favour the reaction of OH radicals with benzene and not with NO_2, despite the fact that the rate constant for the reaction of OH radicals with benzene is approximately 9 times lower than the rate constant for the reaction of OH with NO_2. Nitrogen was selected as the matrix atmosphere of the second series of experiments so that the OH-benzene adduct would react predominantly with NO_2 and not with oxygen in the experiments in which NO_2 was added.

The duration of each irradiation was restricted to 10 minutes to minimize secondary reactions. During the irradiation period, only 6 ± 2% of the initial benzene concentration reacted. The small hydrocarbon consumption caused a great uncertainity in the measurement of the product yields. To aleviate this error source, at each set of conditions at least ten experiments were performed under the same conditions; their average is the reported value. Four photolyses of 1.3×10^{16} molecules/cm^3 benzene without added H_2O_2 were carried out in order to assess the reaction chamber's radical sources, a well known problem of chamber studies. The products formed in the absence of H_2O_2 varied from zero up to 7% of the products measured under the same conditions but in the presence of H_2O_2, indicating no chamber radical sources. The yields reported here were not corrected for the above reason. Dark reactions of benzene with hydrogen peroxide were also carried out, but no benzene consumption or formation of any product was observed.

Benzene and the identified products (phenol, 1,4-benzoquinone, nitrobenzene, and *o*-nitrophenol) were measured on a HP-5890 gas chromatograph equipped with a flame ionization detector after their separation on a 50 m 100% methyl silicone gum capillary column (i.d.: 0.32 mm; film thickness: 1.05 μm). Because of the low concentration of the formed products, the GC was coupled to a Tekmar 5010 GT cryofocuser cooled to −100 °C which enabled the injection of 10–20 ml of sample in the splitless mode. Benzene and the products were identified by matching their retention times with those of authentic compounds. In some selected experiments, the GC was connected to a HP 5971A mass selective detector with the same inlet system which confirmed the identification of benzene and the products. With both detectors, 7–8 more products were observed at retention times shorter than that of benzene. This indicates compounds with a molecular weight smaller than benzene (*i.e.*, aromatic ring cleavage products). The FID was calibrated every eight experiments, and the reported yields are corrected for the relative response of each compound to benzene.

Acknowledgement

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