

1-1-2001

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TESSIER, D.; OGUIC, C.; PINART, J.; and AARON, J. J. (2001) "Usefulness of a Technique Based on Negative Corona Discharge for the Degradation of Selected, Condensed PAHs: Application to the Oxidation of Anthracene and Similar Structures," *Turkish Journal of Chemistry*. Vol. 25: No. 2, Article 4. Available at: <https://journals.tubitak.gov.tr/chem/vol25/iss2/4>

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Usefulness of a Technique Based on Negative Corona Discharge for the Degradation of Selected, Condensed PAHs: Application to the Oxidation of Anthracene and Similar Structures*

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Received 09.10.2000

The usefulness of negative corona discharge for oxidation of condensed polycyclic aromatic hydrocarbons (PAHs), including anthracene, naphthalene and 2,3-benzanthracene, adsorbed on a solid substrate is evaluated. In the case of anthracene, the application of corona discharge under high voltage (10-20 kV) for 10 to 180 min with a current intensity of 5-120 μA in a controlled, humid atmosphere leads to the progressive formation of anthraquinone. A kinetic study of the anthracene oxidation shows that the apparent half-lives range from 5 to 48 min, according to the initial anthracene amount (50-5000 nmol), indicating a reaction order between 0 and 1. The effect of corona discharge current intensity and the role of corona discharge-produced high-speed electrical wind (≈ 10 m/s) are discussed. The efficiency of the solid-phase corona discharge method is found to depend on the adsorption strength of the PAH molecules on the solid substrate and/or their capacity to be sublimated under the influence of electrical wind.

Key Words: PAHs; anthracene; naphthalene; 2,3-benzanthracene; corona discharge; oxidation.

Introduction

Airborne polycyclic aromatic hydrocarbons (PAHs) play an important role as environmental pollutants, because of their carcinogenic and/or mutagenic properties. In general, PAHs are produced during combustion processes of fossil fuel, and they are frequently found in ambient air particles; they can be easily oxidized to PAH-quinones or PAH oxides. Therefore, it seems interesting to use oxidation reactions for the degradation

*This paper has been presented at MBCAC III (3rd Mediterranean Basin Conference on Analytical Chemistry) 4-9 June, 2000 Antalya-Turkey

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of PAHs into less toxic compounds and, possibly, for removing them from the atmosphere. Such a goal could be reached by developing a strategy based on the effects of electrical corona discharge on atmospheric contaminants. Several organic compounds have been submitted to the oxidizing effect of corona discharge in air, and the oxidation products have been characterized in some cases¹⁻⁶.

The present work constitutes a follow-up of our previous studies on the application of corona discharge to oxidation of inorganic and organic pollutants⁶⁻⁷. In this paper, we evaluate the usefulness of negative corona discharge, for oxidation of condensed PAHs such as anthracene, naphthalene and 2,3-benzanthracene on a solid substrate. HPLC with UV absorption detection and GC-MS are utilized for monitoring the degradation process and characterizing the oxidation products. Anthracene is investigated in more detail, as a PAH model; its oxidation kinetic is evaluated under various experimental conditions, and the reaction product is determined.

Experimental

Reagents

Anthracene (Fluka, purity: 98%), anthraquinone (Aldrich, purity: 97%), naphthalene (Prolabo), 1,2-naphthoquinone (Aldrich), 1,4-naphthoquinone (Fluka, purity: 99%) and 2,3-benzanthracene (Aldrich, purity: 98%) were used as received. Dichloromethane (Janssen, spectroscopic grade, 99.8%), ethanol (Merck, spectroscopic grade, 99.9%) and acetonitrile (Prolabo, HPLC grade, 99.8%) were used as solvents. Water was purified by an ion exchange resin and a Millipore system. 25-mm diameter circular filters made of polyvinylidene difluoride (PVDF) (Millipore, HVLP, porosity: 0.45 μm) were used for the deposition of samples.

Instrumentation

The experiments were performed under atmospheric pressure in a 30-L Pyrex reactor, using a point-to-plane corona discharge system, with the same experimental set-up as previously described⁶. Synthetic air (Air Liquide Co., Alphagaz, ref. N50) was sent through electrovalves (Brooks, type 58-78) and 10 mm Teflon tubes. It was humidified by bubblers, kept at constant temperature ($30^{\circ}\text{C} \pm 1^{\circ}\text{C}$) and then passed through two condensers. The reactor included a top and a body tightened with a waterproof joint. It was equipped with a humidity sensor and a thermometer. The air flow rate was 2 L/min, the relative air humidity was between 95 and 100% , and the temperature was maintained at $22^{\circ}\text{C} (\pm 1^{\circ}\text{C})$. The corona discharge was performed in the reactor between two electrodes powered with an Alpha III Brandeburg DC high voltage power supply (10-20 kV). The cathode (point), made of a Pt loop, was centered on the anode, constituted with a stainless steel, circular piece (30 mm diameter) in which was inserted the circular filter. The distance between both electrodes was 10 mm, the intensity of the discharge current varied from 5 to 120 μA , and the discharge time ranged from 1 to 180 min.

UV-visible absorption spectra were recorded on a DMS 200 Varian spectrophotometer. HPLC analyses were accomplished using a Dionex HPLC instrument, equipped with a 201TP54 Vydac column (15 cm length) and a AD20 UV-visible detector set at 251 nm for anthracene, 218 nm for naphthalene and 234 nm for 2,3-benzanthracene. Structural identification was performed on a 1TD800 Finnigan mass spectrometer (MS) coupled to an Intersmat gas chromatograph (GC) and equipped with a CP-SIL-5 capillary column.

Procedures

The experiments were performed as follows. A fixed volume of an ethanol or dichloromethane solution containing a known amount (50, 500 or 5000 nmol) of PAH sample was deposited on a PVDF filter, using a 50 μL syringe. After a 5 min drying time, needed to evaporate the solvent and allow adsorption of the compound, the PVDF filter was inserted into the anode and introduced into the reactor. Then, the PAH sample was submitted to corona discharge, in optimized conditions, at fixed discharge current intensity and discharge time values. After stopping the discharge, the filter was placed in a 5 mL ethanol volume for 10 min, and the remaining PAH and reaction product were extracted. For GC-MS measurements, the solution was concentrated by evaporation.

Results and Discussion

Spectrophotometric study of the anthracene electrical degradation under corona discharge

To determine the effect of corona discharge time on the degradation of anthracene, we performed a series of discharge experiments at different times between 0 and 90 min. Two hundred fifty nanomoles of anthracene were deposited on a PVDF circular filter, and a discharge current intensity of 60 μA was used.

UV-Visible absorption spectra were recorded at the various corona discharge times (Fig.1). Before corona discharge, the anthracene absorption spectrum obtained in ethanol exhibits a main band at 251 nm ($\varepsilon_{\text{max}}=2.7 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) and a much weaker band with a maximum at 356 nm ($\varepsilon_{\text{max}}=7.3 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$), characterized by a fine, well-resolved, vibrational structure. During the discharge, an important and regular decrease in the absorbance of both bands was observed with increasing discharge times, which indicates that the amount of anthracene spotted on the filter diminishes with the duration of the corona discharge. Taking into account our previous results on the transformation of fluorene into fluorenone under corona discharge⁶, we can expect that the main oxidation product of anthracene should be anthraquinone. However, because of the similarity of anthracene and anthraquinone spectra (anthraquinone presenting two absorption bands at 251 nm, $\varepsilon_{\text{max}}=1.5 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 321 nm, $\varepsilon_{\text{max}}=2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), no definitive conclusion on the possible formation of anthraquinone can be reached at this stage.

Gas chromatography mass spectrometry (GC-MS) analysis

We investigated by GC-MS fifteen anthracene samples of 2500 nmol which were submitted to corona discharge (current intensity : 60 μA) for 60 min, extracted with ethanol and heated, allowing solvent evaporation. Two main peaks were obtained at elution times of 610 s and 735 s. The mass spectra show that these two peaks correspond, respectively, to anthracene ($m/z = 178$) and anthraquinone ($m/z = 208$). This characterization was also checked by comparing these mass spectra with those of the authentic compounds, measured independently.

Kinetic studies of anthracene oxidation

The decrease in anthracene and concomitant formation of anthraquinone with time observed when the samples were submitted to corona discharge (current intensity = 60 μA) were monitored using HPLC with

UV spectrophotometric detection. The peaks corresponding to anthracene and anthraquinone were observed at 10.6 and 5.2 min, respectively. HPLC calibration curves, based on standard solutions of the authentic compounds not submitted to corona discharge, were used to determine the respective amounts of anthracene and anthraquinone.

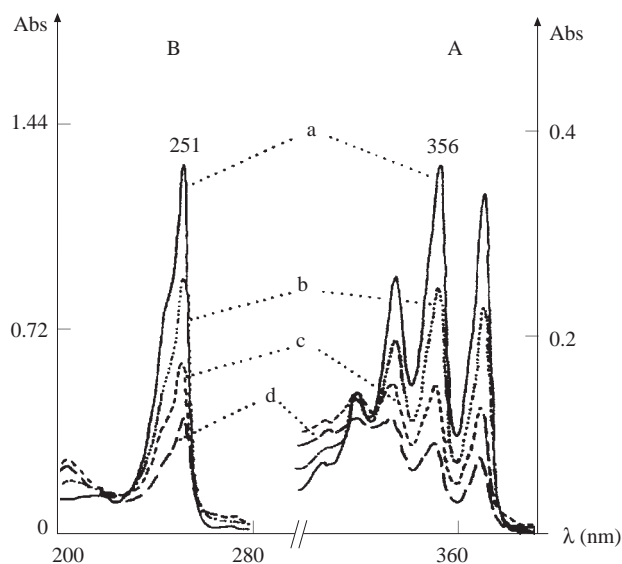


Figure 1. UV absorption spectra of 250 nmol anthracene submitted to the following corona discharge times (in min): (a) 0; (b) 15; (c) 60; (d) 90. Discharge current intensity = $60 \mu\text{A}$. Spectra A and B correspond respectively to a 5.10^{-5} and a 5.10^{-6} M anthracene ethanolic solution.

The kinetics of anthracene degradation and anthraquinone formation were investigated for initial anthracene amounts of 50, 500 and 5000 nmol. Figures 2-4 present the plots of recovered amounts of anthracene and anthraquinone (in nmol) *versus* discharge time (in min). In all cases, the anthracene decrease obeyed exponential curves, with apparent half-life ($t^{1/2}$) values varying between 5 and 48 min, for anthracene initial amounts going from 50 to 5000 nmol. In other words, the kinetic of anthracene degradation is much faster for small amounts than for large amounts of anthracene. The reaction order is between 0 and 1, since the variation of $t^{1/2}$ is not proportional to the initial anthracene amount.

As can be seen in Figs. 2-4, the anthracene degradation curves are characterized by a plateau region reached after discharge times of 120-180 min, corresponding to 1.2, 10 and 73% of remaining anthracene, for initial amounts of 50, 500 and 5000 nmol, respectively. The curves of anthraquinone formation also reach a plateau region, with an anthraquinone yield ranging from 38 to 7% , at a 120 min discharge time, for initial anthracene amounts of between 50 and 5000 nmol.

Effects of the electrical wind

It is worthwhile to note that, in the plateau region of the curves, the remaining anthracene and anthraquinone nmol number is smaller than the initial amount of anthracene. For example, after a discharge time of 120 min, a total amount of about 250 nmol of anthracene + anthraquinone remains , whereas the initial anthracene amount is 500 nmol (Fig. 3). This indicates a significant loss of mass during the oxidation reaction. This phenomenon is comparable to the incomplete transformation of fluorene into fluorenone under corona

discharge that we observed previously⁶. It may be rationalized as follows: very probably, oxidation products (other than anthraquinone) not detectable by UV-visible absorption are formed under the discharge and, also, a significant amount of anthracene and/or anthraquinone is removed from the circular filter by the “electrical” wind produced by corona discharge. Indeed, the elastic and inelastic collisions occurring between the electrons, and neutral and charged molecular species are known to produce an atmospheric depression in the discharge region located near the dissymmetric electrodes; as a consequence, a strong and fast “electrical” wind is created with a speed of about $10 \text{ m}\cdot\text{s}^{-1}$ ⁸. It can be postulated that anthracene and/or anthraquinone solid particles adsorbed on the filter are either partially moved by the electrical wind or sublimated.

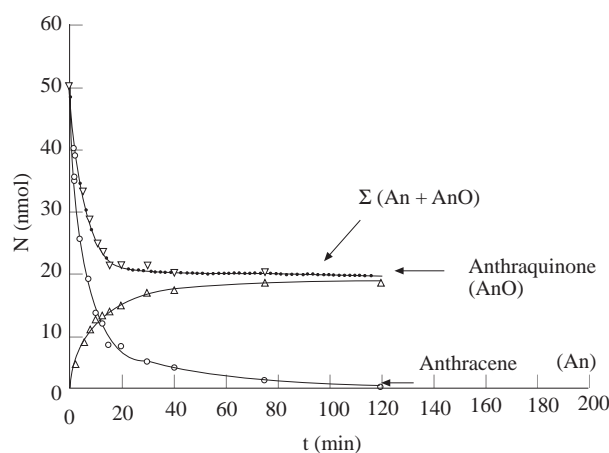


Figure 2. Plots of the anthracene (An), anthraquinone (AnO) and (An + AnO) amounts *versus* discharge time for a current intensity of $60 \mu\text{A}$. Initial anthracene amount: 50 nmol.

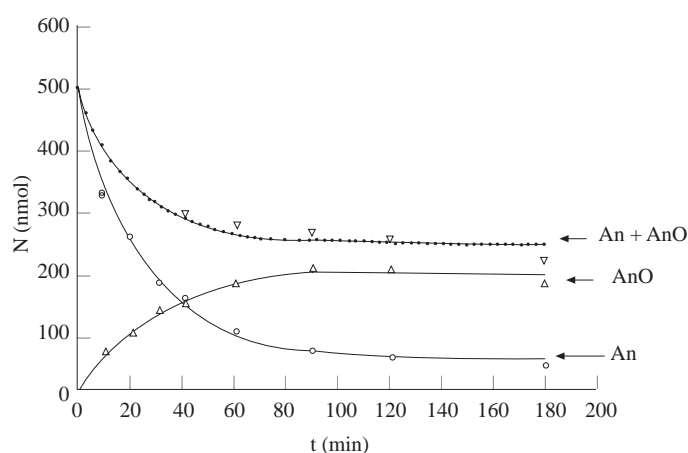


Figure 3. Plots of the An, AnO and (An + AnO) amounts *versus* discharge time for a current intensity of $60 \mu\text{A}$. Initial anthracene amount: 500 nmol.

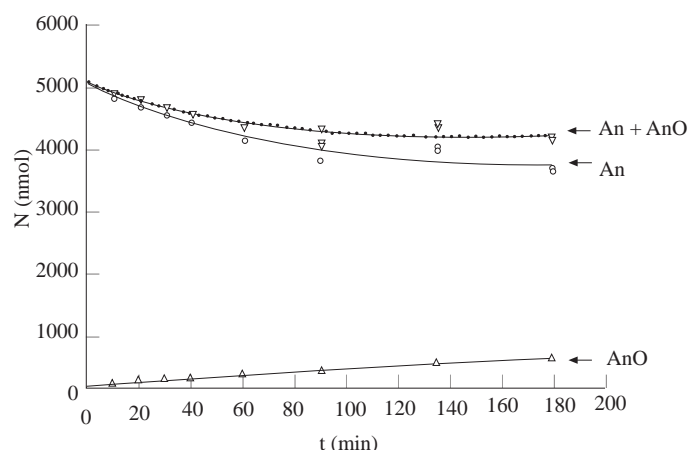


Figure 4. Plots of the An, AnO and (An + AnO) amounts *versus* discharge time for a current intensity of 60 μA . Initial anthracene amount: 5000 nmol.

Effect of the corona discharge current intensity

We studied the effect of the corona discharge current intensity by submitting 500 nmol of anthracene to varying current intensities (5-120 μA) during a discharge time of 30 min. The decrease in anthracene and formation of anthraquinone were monitored by HPLC.

Figure 5 shows the plots of the number of nmol of anthracene and anthraquinone *versus* the current intensity. As can be seen, the anthracene amount decreases whereas the anthraquinone amount increases with intensity. This behavior can be attributed to the production of larger amounts of HO^\bullet radicals for higher discharge current intensity values; as a result, more anthracene molecules are attacked and more anthraquinone molecules are formed. As already noted, the loss of mass deduced from the curve corresponding to the variation of the sum of anthracene and anthraquinone amounts can be explained by the effect of electrical wind. Finally, our study indicates also that the optimal range of corona discharge current intensity values is located between 40 and 60 μA . The use of larger intensities (and larger electrical energies) for the corona discharge would not improve the degradation of anthracene, nor the formation of anthraquinone.

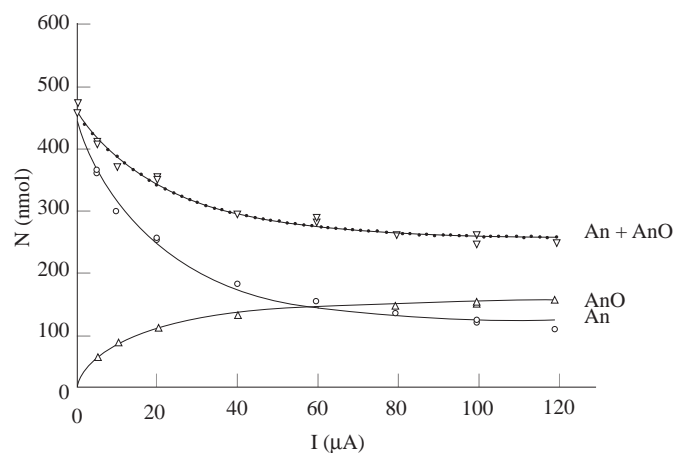


Figure 5. Plots of the An, AnO and (An + AnO) amounts *versus* current intensity. Discharge time = 30 min. Initial anthracene amount: 500 nmol.

Effect of corona discharge on anthraquinone

In order to examine whether anthraquinone could be also degraded under corona discharge, we performed several corona discharge experiments on 250 nmol of this compound deposited on a PVDF filter, using a current intensity of 60 μA , for 40 min. The anthraquinone samples were analyzed by HPLC with UV absorption detection. No change in the anthraquinone amount was observed and no reaction product was detected under these experimental conditions. These results suggest that anthraquinone is stable under corona discharge and is not sublimated, probably because anthraquinone molecules are strongly adsorbed at the surface of the solid substrate.

Corona discharge effect on the degradation of other PAHs

We also carried out a similar study on the effect of corona discharge on the degradation of other PAHs close to anthracene, including naphthalene and 2,3-benzanthracene.

In the case of naphthalene, a series of discharge experiments were performed at different times between 0 and 15 min, using a 60 μA current intensity. Five hundred and 5000 nmol of naphthalene were deposited on a PVDF circular filter. Exponential curves of naphthalene amount *versus* discharge time were obtained, with $t^{1/2}$ values of 2.5-2.8 min; after 15 min of corona discharge application, 96 to 98% of naphthalene disappeared. However, GC-MS and HPLC analysis did not show evidence of the formation of 1,2-naphthoquinone, 1,4-naphthoquinone or other oxidation reaction products. These results indicate that a part of the naphthalene deposit as well as the oxidation products eventually formed during corona discharge are probably removed from the solid state substrate by the electrical wind produced by corona discharge and/or sublimated. Indeed, naphthalene molecules might be weakly adsorbed on the solid substrate, and they are well known to easily sublimate.

In the case of 2,3-benzanthracene, a series of corona discharge experiments were carried out on 150 nmol of the compound (deposited on a PVDF filter) for times ranging from 0 to 90 min, using a 60 μA current intensity. We observed a relatively slow exponential decrease in the initial 2,3-benzanthracene amount with time ($t^{1/2} \sim 1\text{-}2\text{h}$) and the concomitant formation of a reaction product. Because of solubility problems, a GC-MS study could not be performed to characterize this new product.

Conclusion

We can conclude from our work that anthracene is oxidized into anthraquinone under corona discharge in humid atmosphere and that no formation of anthraquinone by-product occurs. However, the relatively small recovery values found for anthraquinone under various conditions suggests a significant role for electrical wind, which would partially move away or sublimate anthracene and/or anthraquinone during the corona discharge processes. Similar corona discharge studies, performed on naphthalene and 2,3-benzanthracene, confirm the importance of the sublimation phenomenon in addition to the oxidation reaction of PAHs. Therefore, the efficiency of solid-phase corona discharge as a decontamination method seems to depend mainly on the adsorption strength of the PAH molecules on the solid substrate and/or their capacity to be sublimated under the influence of electrical wind.

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