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# On the Mechanism of Indeno[1,2,3-*c*,*d*]-pyrene Ozonation

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**Summary.** Calculations on the strongly cancerogenic indeno[1,2,3-*c*,*d*]pyrene and all its possible primary and secondary ozonides by the MNDO method indicate the breaking of the $C_{21}$–$C_{22}$ bond of the pyrene fragment as the energetically most favourable first step of the oxidative degradation. Localization energies calculated within the simple *Hückel* model predict that the attack of the $C_{21}$–$C_{22}$ pair by ozone is most probably also kinetically the most preferred reaction path. The rather low localization energy of $C_{20}$ in the pyrene fragment indicates the possibility of competitive reactions between ozonolysis and the formation of phenols and quinones. The theoretical results are supported by experimental findings on the ozonation of indeno[1,2,3-*c*,*d*]pyrene in aqueous medium.

**Keywords.** Indeno[1,2,3-*c*,*d*]pyrene; Ozonation; MNDO-method

### Über den Mechanismus der Ozonierung von Indeno[1,2,3,*c*,*d*]pyren

**Zusammenfassung.** MNDO-Berechnungen über das krebserregende Indeno[1,2,3-*c*,*d*]pyren und seine möglichen primären und sekundären Ozonide deuten auf die Brechung der $C_{21}$–$C_{22}$-Bindung des Pyrenresters als die energetisch günstigste erste Stufe des oxidativen Abbaus hin. Die nach dem einfachen *Hückel*-Modell berechneten Lokalisierungsenergien zeigen, daß der Ozonangriff an das $C_{21}$–$C_{22}$-Paar vielleicht auch der kinetisch bevorzugte Weg ist. Die zu kleine Lokalisierungsenergie beim $C_{20}$-Atom im Pyrenrest indiziert mögliche Konkurrenz zwischen der Ozonolyse und der Bildung von Phenolen und Chinonen. Die theoretischen Ergebnisse werden durch experimentelle Resultate über die Ozonierung von Indeno[1,2,3-*c*,*d*]pyren in wäßrigem Medium bestätigt.

## Introduction

Some polycyclic aromatic hydrocarbons are strongly cancerogenic. In this respect, benzopyrene and indeno[1,2,3-*c*,*d*]pyrene are considered as the most toxic compounds [1]. The content of the components in many waste and drinking waters considerably exceeds the utmost allowed concentration (UAC) [2, 3]. Therefore, the investigation of their oxidative degradation is an important task. One of the promising methods in this respect is ozonation [3]. To our knowledge, no results on the ozonation of indeno[1,2,3-*c*,*d*]pyrene and the possible products of this process are reported in the literature.

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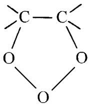
One of the most important questions is which atoms of the indeno[1,2,3-*c*,*d*]pyrene are affected first by ozone at the onset of the degradation process. This will determine the mechanism and the products of the reaction. In this work we have tried to contribute to the solution of that question by model calculations.

## Methods

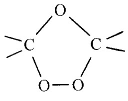
All calculations in this work have been performed within the semiempirical *Hartree-Fock* MNDO method [4] as implemented in the General Atomic and Molecular Electronic Structure System (GAMESS) by *M. W. Schmidt et al.* [5]. Model parameters are given elsewhere [4]. Using this method, all possible primary (**1**) and secondary (**2**) ozonides of indeno[1,2,3-*c*,*d*]pyrene (Fig. 1) have been calculated. Energies of localization of electrons on single carbon atoms or pairs of C–C atoms within the aromatic system are calculated using the simple *Hückel* model.

## Results and Discussion

The minimization of the total energy for the ground state of indeno[1,2,3-*c*,*d*]pyrene within the MNDO method leads to an optimum geometry whose C–C bond lengths are given in Fig. 2. In parentheses we also indicate the bond lengths derived *via* energy minimization for benzene and pyrene separately. With the only exception of the $C_9$–$C_{10}$ bonds, the geometric changes in the direction from benzene and pyrene to indenopyrene are not considerable. The $C_9$–$C_{10}$ bond gets by about 0.05 Å longer together with the newly formed $C_9$–$C_7$ and $C_1$–$C_{10}$ bonds,



**1**



**2**

**Fig. 1.** Primary (**1**) and secondary (**2**) ozonides

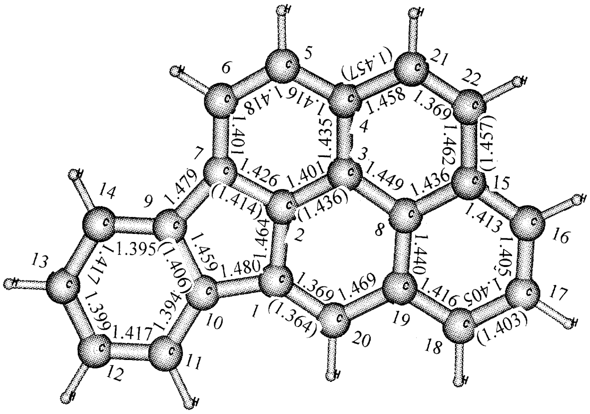


**Fig. 2.** C–C bond lenghts (Å) of indeno[1,2,3-*c*,*d*]pyrene as obtained *via* geometry optimization within the semiempiric SCF-MNDO method; for the sake of comparison, C–C bond lenghts for the ground state energy minimum of the separate benzene and pyrene fragments are also given (in parentheses)

which are considerably longer compared to the normal C–C aromatic bond (1.406 Å in benzene). It is interesting to note that the pyrene system itself undergoes only minor changes on condensation.

Within the MNDO method, the energetics of reactions (1) and (2) (in a thermodynamical sense, $\Delta H = \Delta U$, $T = 0\,\mathrm{K}$) are calculated as the difference between the ground state energies of the products and the energies of indeno[1,2,3-*c*,*d*]pyrene and ozone (3).

$$\text{Indeno}[1,2,3 - c,d]\text{pyrene} + \mathrm{O_3} \rightarrow \text{primary ozonide (type}\mathbf{1}) \tag{1}$$

$$\text{Indeno}[1,2,3 - c,d]\text{pyrene} + \mathrm{O_3} \rightarrow \text{secondary ozonide (type}\mathbf{2}) \tag{2}$$

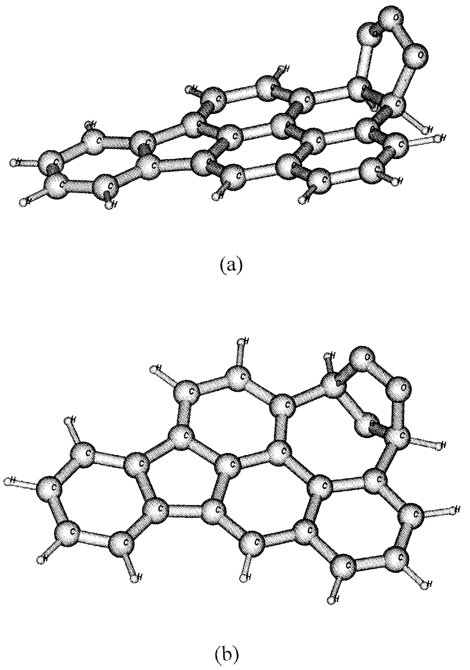
$$\Delta U = E(\mathrm{C_{22}H_{12}O_3}) - E(\mathrm{C_{22}H_{12}}) - E(\mathrm{O_3}) \tag{3}$$

All energies are calculated for geometries minimizing the total energy. For that purpose, a geometry optimization of ozone and the primary and secondary ozonides for all possible modes of attack with respect to cycloaddition of ozone to

**Table 1.** Energies of formation (eV) of primary and secondary ozonides and energies of localization of pairs of neighbouring C-atoms and single C-atoms of indeno[1,2,3-*c*,*d*]pyrene; T and S refer ternary and secondary carbon atoms, respectively

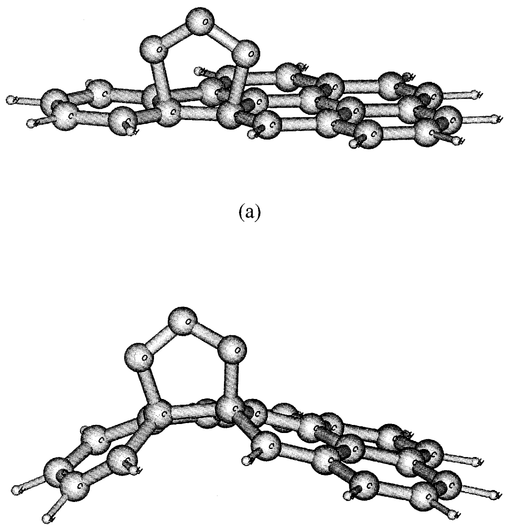
| Pair C–C | Type | $\Delta H$ (primary) $C_{22}H_{12}O_3$ | $\Delta H$ (secondary) $C_{22}H_{12}O_2O$ | $E_{\mathrm{loc}}$ (bond) | $E_{\mathrm{loc}}$ (atom) | |
|---|---|---|---|---|---|---|
| 21–22 | S-S | −2.240 | −4.471 | 1.050 | 4.587 | 4.388 |
| 16–17 | S-S | −1.702 | −3.893 | 2.236 | 4.072 | 5.034 |
| 17–18 | S-S | −1.708 | −3.906 | 2.208 | 5.034 | 4.067 |
| 11–12 | S-S | −1.624 | −3.981 | 4.289 | 4.750 | 4.773 |
| 12–13 | S-S | −1.826 | −4.169 | 4.408 | 4.773 | 4.808 |
| 13–14 | S-S | −1.621 | −3.982 | 4.290 | 4.808 | 4.710 |
| 5–6 | S-S | −1.782 | −4.198 | 4.280 | 4.367 | 4.539 |
| 19–20 | T-S | −0.228 | −2.805 | 3.956 | 5.269 | 3.738 |
| 15–22 | T-S | −0.168 | −2.612 | 3.997 | 5.263 | 4.388 |
| 10–11 | T-S | −1.390 | −4.057 | 4.438 | 4.957 | 4.750 |
| 9–14 | T-S | −1.390 | −4.050 | 4.437 | 5.004 | 4.710 |
| 6–7 | S-T | −1.352 | −4.013 | 4.392 | 4.539 | 4.749 |
| 4–5 | T-S | −1.261 | −3.998 | 4.297 | 4.897 | 4.367 |
| 4–21 | T-S | −0.135 | −2.598 | 4.021 | 4.897 | 4.587 |
| 1–20 | T-S | −1.760 | −4.360 | 1.410 | 4.958 | 3.738 |
| 18–19 | S-T | −1.092 | −3.671 | 2.742 | 4.065 | 5.269 |
| 2–7 | T-T | −1.220 | 1.084 | 3.180 | 5.198 | 4.749 |
| 2–3 | T-T | −0.618 | 1.227 | 3.328 | 5.198 | 5.332 |
| 1–10 | T-T | 1.533 | −1.072 | 5.738 | 4.958 | 4.957 |
| 7–9 | T-T | 1.452 | −1.247 | 5.544 | 4.749 | 5.004 |
| 3–8 | T-T | 0.285 | 1.169 | 4.087 | 5.332 | 5.113 |
| 1–2 | T-T | −0.262 | 2.149 | 3.984 | 4.958 | 5.198 |
| 8–15 | T-T | −0.500 | −0.258 | 4.186 | 5.113 | 5.263 |
| 9–10 | T-T | −1.454 | −0.209 | 4.015 | 5.004 | 4.957 |
| 8–19 | T-T | −0.556 | −0.587 | 4.137 | 5.113 | 5.269 |
| 3–4 | T-T | −0.368 | 0.198 | 4.172 | 5.332 | 4.987 |

corresponding pairs of neighbouring carbon atoms (26) was performed. The results with the $\Delta U$ values for primary and secondary ozonides are presented in Table 1. The addition of the ozone molecule to indeno[1,2,3-*c*,*d*]pyrene yields the most stable products for the $C_{21}$–$C_{22}$ pair. The destructive oxidation of indeno pyrene from a thermodynamic point of view is predicted to start with the pair. The geometries for the $C_{21}$–$C_{22}$ ozonides, both primary and secondary, are presented graphically on Figs. 3a and 3b, respectively. The normal coordinate analysis performed using force field parameters derived from the same model (MNDO) hamiltonian yields positive vibrational frequencies which suggest that both species have to be regarded as stable products rather than as transition states. The results show that the addition to the ternary carbon atoms ($C_1$–$C_{10}$) would be extremely unfavourable (in a thermodynamic sense). This is illustrated in Figs. 4a and 4b. Fig. 4a shows the ozone molecule at the moment of attack without change of the other bond and can be roughly interpreted as a transition state in which the $\pi$-electronic $C_1$–$C_{10}$ bond is still not broken, whereas the C–O bonds are not yet formed. In Fig. 4b, this transition state has relaxed with an elongation of the C–C bond from 1.48 Å to 1.55 Å and a considerable deviation of the molecule from planarity due to the switch of the $C_1$ and $C_{10}$ atoms from $sp^2$ to $sp^3$ hybridization state. The deviation from planarity is connected with a considerable lost of energy accompanying the newly formed $\sigma$-bonds; the reaction is calculated to be endothermic. An analogous result is obtained for cycloaddition to $C_7$ and $C_9$ (Fig. 1, Table 1). It is interesting to note that the attack of two secondary carbon atoms or a pair of a secondary and a ternary carbons leads to secondary ozonides which are lower in energies compared to the primary ones. The same conclusion holds true


(a)

(b)

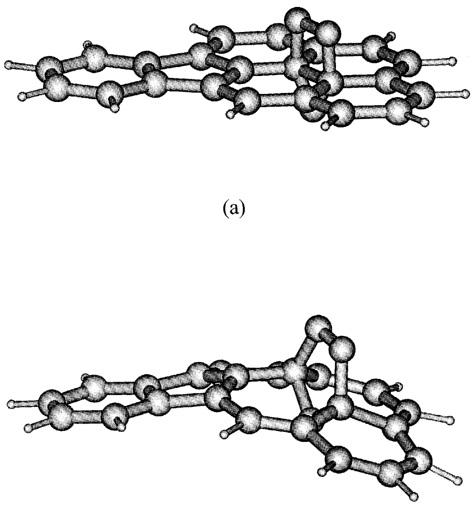
**Fig. 3.** Structural views of the most stable calculated ($C_{21}$–$C_{22}$) primary (a) and secondary (b) ozonides of indeno[1,2,3-*c*,*d*]pyrene



(a)

(b)

**Fig. 4.** Primary ozonides before (a) and after (b) relaxation of bond lengths and bond angles resulting from the pair of carbon atoms ($C_1$–$C_{10}$) connecting the benzene and pyrene fragments



(a)

(b)

**Fig. 5.** Secondary ozonides before (a) and after (b) relaxation of bond lengths and bond angles resulting from the pair of ternary carbon atoms ($C_3$–$C_8$) within the pyrene fragment

for the pair of ternary C-atoms $C_7$–$C_9$ and $C_1$–$C_{10}$, connecting the benzene and pyrene fragments. For the pairs of ternary C-atoms included in the pyrene fragment, secondary ozonides are calculated in all cases to have higher energy than the primary ones. The reason for this may be the heavy disturbance of the $\pi$-electronic system, connected with the corresponding loss of energy which is more pronounced for the secondary than for the primary ozonides. This is illustrated in Figs. 5a and 5b for the primary and secondary ozonides, respectively. In this case

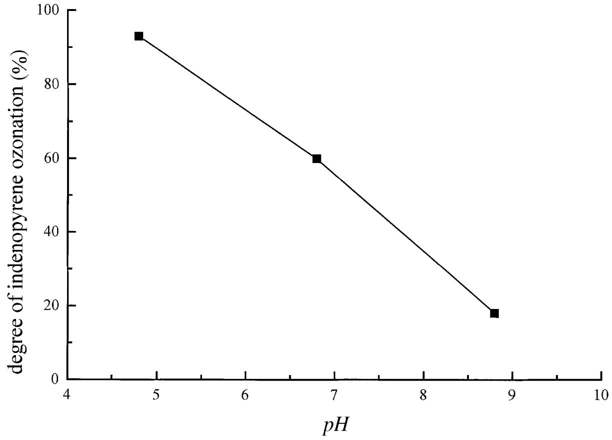


**Fig. 6.** Dependence of degree of ozonation of indeno[1,2,3-*c*,*d*]pyrene on the *pH* value; reaction conditions: ozone concentration, 5.5 g/m$^3$; indeno[1,2,3-*c*,*d*]pyrene concentration, 1.5 mg/l; temperature, 22°C; buffer solutions based on $K_2HPO_4$ and $KH_2PO_4$; 8 ml/l methanol; reactor volume, 500 ml; oxygen flow, 3.8 l/h

the $C_3$ and $C_8$ atoms, which play a central role in the $\pi$-electronic system of the pyrene fragment, become partly (in the primary ozonide) or completely (in the secondary ozonide) excluded from the conjugated system.

Within the so-called localization theory [6] and the *Hückel* model we calculated the energy needed to localize $\pi$-electrons on a pair of neighbouring C-atoms or on single atoms. The localization energy is derived as the difference between the total energies of the localized fragments and the molecule without localization. For localizations on bonds or on atoms, Eqs. (4) and (5) are valid, respectively.

$$E_{\mathrm{loc}}(\mathrm{bond}) = E(\mathrm{C}_{20}\mathrm{H}_{22}) + E(\mathrm{C}_2) - E(\mathrm{C}_{22}\mathrm{H}_{22}) \tag{4}$$

$$E_{\mathrm{loc}}(\mathrm{atom}) = E(\mathrm{C}_{21}\mathrm{H}_{22}) + E(\mathrm{C}) - E(\mathrm{C}_{22}\mathrm{H}_{22}) \tag{5}$$

The calculated energies are used here as a measure of the activated complex energy in transition state theory and allow analysis of the possibilities in the case of several competitive reactions. The energies of localization on bonds and atoms are included in Table 1. As a main result, the lowest localization energy is calculated for the pair $C_{21}$–$C_{22}$, which is also the one calculated to yield the most stable products of ozonation. In other words, the primary and secondary ozonides with participation of atoms $C_{21}$ and $C_{22}$ are not only lowest in energy, but are also those which are most easily assessible kinetically.

Another interesting result is that the localization at an atom is lowest for $C_{20}$, whereas localization on a bond is lowest for the $C_{21}$–$C_{22}$ pair, *i.e.* competition between ozonolysis (leading to dialdehydes) and formation of phenols and quinons occurs.

As a conclusion, the most probable attack of ozone on indenopyrene is the breaking of the $C_{21}$–$C_{22}$ bond with formation of primary and secondary ozonides. It is also interesting that under certain conditions these could be regarded as the final products.

The theoretical results are supported by preliminary experimental data based on a study concentrating on the first stage of ozonation of indenopyrene. Figure 6 presents the dependence of ozonation on the *pH* value.

The experiments on the ozonation of indeno[1,2,3-*c*,*d*]pyrene show that the oxidation rate sharply decreases in the alkalic region. As far as the effect of the radical mechanism increases with the *pH* value [7], it should be supposed that the oxidation of indeno[1,2,3-*c*,*d*]pyrene would proceed mainly by direct interaction with ozone, which is in coincidence with the results of the above theoretical predictions.

In further experimental studies we will follow more closely the other products resulting from the oxidative treatment of indeno[1,2,3-*c*,*d*]pyrene.

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