

Communications to the Editor

Preparation of Decachlorocorannulene and Other Perchlorinated Fragments of Fullerenes by Electrical Discharge in Liquid Chloroform

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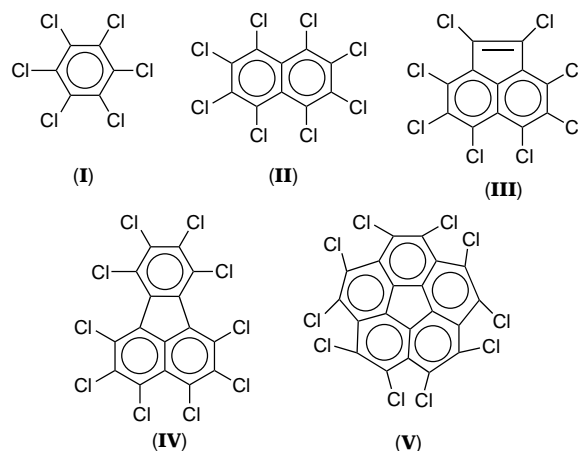
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Since the pioneering work of Kratscher and Huffman,¹ C₆₀ and other fullerenes have been prepared by arc discharge between graphite electrodes in helium atmosphere. Grosser and Hirsch² vaporized graphite under similar conditions but in the presence of (CN)₂ and obtained a series of dicyanopolyyne products. When experiments were carried out in Cl₂ atmosphere, hexachlorobenzene and other perchlorinated compounds appeared as the main products.² Recently, we have performed the arc discharge experiments in a different way where the discharge reaction is allowed to proceed in liquid rather than in the gas atmosphere. In this paper, we report the discharge reaction performed in liquid chloroform. Various reaction products have been obtained, from which decachlorocorannulene and some other perchlorinated aromatic compounds have been separated and characterized. The results in this work are of significance in understanding the formation mechanism of fullerenes, as it will be shown that all of the characterized products are perchlorinated fragments of C₆₀.

The experiment was performed in a 500-mL three-necked flask. The reagent is 300 mL of chloroform which was purified before the reaction to eliminate the possible contamination (including aromatic compounds). Purity of the reagent was examined by GC-MS analysis. During the reaction, purified nitrogen gas was bubbled through the reagent to preserve an inert atmosphere. Two copper electrodes, mounted on the each of the two side necks of the flask, were immersed into the liquid at a fixed angle. The gap between the two electrodes was about 1 mm. An ac voltage over 10 kV in 20 kHz was applied to the electrodes. The stable arc discharge could be maintained by adjusting either the applied voltage or the gap distance between the electrodes. The arc current of 20–50 mA was typical in the present work. A large amount of acidic gases were produced during the reaction which was characterized as the mixture of HCl and Cl₂. A deep red-brown solution was obtained after a 5-h discharge. After the remaining solvent was removed by vacuum evaporation, 3–4 g of residue was collected. About 40% of the residue was sublimated at 160 °C as colorless needle crystals (I). The remainder was dissolved in benzene and separated by neutral Al₂O₃ column chromatography, with petroleum ether / benzene in different ratios as the elute. Several fractions have been collected with different yields: 8% light yellow needle crystal (II), 20% orange needle crystal (III), 12% green feather crystals (IV), and 8% brown powder (V). Separation and characterization of other products, which amount to more than 10% of the residue, are still in progress.

Characterization of the above obtained species were carried out at different stages. None of the signals that appeared in the ¹H-NMR spectra can be assigned to any of the characterized products. It can, therefore, be concluded that the products



consist of chlorine and carbon only. The reacted solution was analyzed by GC-MS before the column chromatographic separation, and various products with low boiling points, such as C₂Cl₄, C₃Cl₆, C₄Cl₈, C₄Cl₆, and C₅Cl₆, were detected.

Chemical formulas of the separated products I–V were determined by mass spectrometry. From the masses and the isotopic patterns of molecular ion peaks in the recorded mass spectra,³ the products can be assigned to C₆Cl₆ (I), C₁₀Cl₈ (II), C₁₂Cl₈ (III), C₁₆Cl₁₀ (IV), and C₂₀Cl₁₀ (V), respectively. When the IR and UV–vis data of the products⁴ were compared with those of known compounds, products I–IV could be further identified as hexachlorobenzene (I), octachloronaphthalene (II),^{5,6} octachloroacenaphthylene (III),⁷ and decachlorofluoranthene (IV),^{8,9} respectively. In addition, XRD results of product I are consistent with that of the known hexachlorobenzene compound.

Although the molecular formula C₂₀Cl₁₀ may correspond to a few structural isomers, the decachlorocorannulene seems to be most likely. Scott reported the preparation of this compound, but no spectral data are available.¹⁰ Further investigation using ¹³C- and ³⁵Cl-NMR spectroscopy was, therefore, carried out in the present work in addition to the IR and UV–vis measurements.¹¹ There are three peaks in the recorded ¹³C-NMR

(3) Mass peaks of the molecular ions in *m/z* (%): product I 282 (51.43), 284 (100.00), 286 (76.58), 288 (33.14), 300 (6.29); product II 400 (32.14), 402 (85.71), 404 (100.00), 406 (64.29), 408 (28.57); product III 432 (4.14), 430 (23.99), 428 (62.00), 426 (100.00), 424 (80.12), 422 (27.76); product IV 554 (4.80), 552 (20.38), 550 (50.66), 548 (98.67), 546 (100.00), 544 (66.58), 542 (19.09); product V 590 (20.50), 592 (66.67), 594 (100.00), 596 (88.89), 598 (51.85), 600 (20.74), 602 (17.28).

(4) Spectroscopic data: product I UV–vis/CCl₄ λ_{max} = 272 nm, IR 1340 (s), 1295 (m), 715 (w), 690(s); product II UV–vis/C₂H₅OH λ_{max} = 270 nm, IR 1730 (w), 1520 (s), 1414 (m), 1355 (w), 1290 (s), 1270 (s), 1250 (s), 1220 (w), 1165 (m), 1060 (w), 965 (m), 860 (w), 780 (w), 750 (w), 690 (m), 665 (m); product III UV–vis/C₆H₁₂ λ_{max} = 365 nm, IR 1555 (m), 1495 (m), 1415 (m), 1365 (m), 1290 (m), 1230 (m), 1160 (m), 1120 (s), 700 (m); product IV UV–vis/C₆H₆ λ_{max} = 220 nm, IR 1525 (w), 1370 (s), 1350 (m), 1330 (m), 1300 (s), 1265 (m), 1150 (s), 1030 (m), 915 (m), 895 (m), 805 (m), 690 (m).

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(11) Spectroscopic data of product V: UV–vis/C₆H₅CH₃ λ_{max} = 290 nm; IR 1720 (m), 1540 (m), 1455 (s), 1360 (s), 1340 (m), 1290 (m), 1270 (m), 1250 (m), 1150 (m), 1090 (m), 1010 (w), 950 (s), 710 (m).

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spectra, 129.62, 128.37, and 128.16 ppm, with a ratio of 2:1:1 and a single peak in ^{35}Cl -NMR, 507.36 ppm, which is consistent with the structure of decachlorocorannulene.

The discharging reaction in liquid was expected to be complex. Surprisingly, however, the experimental results of the present work show that the reaction products are quite selective: All of the products that have been characterized so far are perchlorinated polycyclic compounds. In fact, we have also performed a similar experiment in CCl_4 , and the same products were obtained. Among various possibilities is that dichlorocarbene is the reaction intermediate which aggregates to form the observed products. Other radical pathways may also be envisioned. When the formation enthalpies of $:\text{CCl}_2$ and $:\text{CHCl}$ are compared with that of CHCl_3 ,¹² it can be shown that formation of the former is thermodynamically favorable. Therefore, hydrogen can be ruled out in composition from all of the products.

It is clear from the structural analysis that all of the characterized products of the discharging reaction are aromatic compounds. Their structural stability is also demonstrated by the EI mass spectra showing predominant signal intensity of the molecular ions. Under electron bombardment, these molecular ions lose chlorine atoms one by one with carbon

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frameworks kept unchanged. Another interesting structural feature is that rings of the product compounds tend to pack together rather than forming a relatively simple polycyclic structure like that in anthracene. In particular, the occurrence of five-membered-ring is noteworthy as it is essential for the formation of C_{60} and other fullerenes. In fact, all of the characterized products in the present work can be considered as the perchlorinated intermediates in forming C_{60} . Therefore, the significance of the reaction is not limited to the synthesis of the decachlorocorannulene and other perchlorinated products; it is also helpful to the understanding of the formation mechanism of fullerenes.

Although the reagent of the experiment, chloroform molecules, contain a single carbon atom only, in the discharging reaction, they serve as C_1 building block, which aggregate to structures that are parts of the fullerene framework. Hence, the extension of the discharging reaction from the gas phase into the liquid media allows the synthesis of interesting and novel compounds. The experimental results reported in this paper has demonstrated the potential ability of the technique.

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