EPR study of the reaction of C_{60} with chlorine dioxide: experimental evidence for the formation of the C_{60} radical cation

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The interaction of chlorine dioxide with fullerene C_{60} affords a brown precipitate, and its EPR spectrum exhibits an asymmetric singlet signal ($g = 2.0029$, $\Delta H_{pp} = 0.2$ mT) tentatively assigned to the fullerene radical cation.

With the development of a large-scale method for preparing fullerenes,[1] the investigation of chemical properties of C_{60} became possible. It was found that C_{60} was reversibly reduced accepting up to six electrons with formation of the radical anions $C_{60}^{\cdot n-}$ or the anions C_{60}^{n-}.[2] On the other hand, oxidation of the fullerene is limited by the transfer of only one electron, yielding the radical cation $C_{60}^{\cdot +}$. The formation of $C_{60}^{\cdot +}$ in solution was observed upon oxidation of ground-state[3,4] or triplet[5–7] fullerene, as well as upon disproportionation of two $^3C_{60}$ molecules.[8] Chlorine dioxide[9,10] is a mild one-electron oxidant [$E(ClO_2/ClO_2^-) = 0.94$ V, NHE, water[11]], which readily oxidises polyaromatic and heteroaromatic compounds into corresponding radical cations.[12] At the same time, the redox potential of ClO_2 is insufficient for the direct oxidation of ground-state fullerene [$E(C_{60}^{\cdot +}/C_{60}) = 2.00$ V, NHE, benzonitrile[13]].

Here we report the first investigation of a reaction between chlorine dioxide and fullerene C_{60}. A solution of ClO_2 in benzene (0.03–0.14 M) was added to a C_{60} solution in the same solvent (0.014 M); the ratios $[ClO_2]_0$:$[C_{60}]_0$ varied from 5:1 to 125:1 (25 °C). The solution turned opalescent, and a brown precipitate was formed 10–30 s after the reactants were mixed. At the instant the precipitate was formed, a flash of visible (350–600 nm) and IR (1000–1300 nm) chemiluminescence was observed (Figure 1). The EPR spectrum of the precipitate exhibits an asymmetric singlet with $g = 2.0029\pm0.0002$, $\Delta H_{pp} = 0.2$ mT and the a/b ratio 0.75 (Figure 2). Similar singlets of the anti-Dysonian type were observed in the EPR spectra of hole-conduction polymers.[14,15] The EPR spectra of a sample that was prepared *in situ* and of a sample isolated by centrifugation and dried in a vacuum were identical. No considerable EPR signals were detected in the solution over the precipitate. The estimated yield of spins is 0.3% with respect to the initial fullerene.

Chlorine dioxide was completely consumed in the reaction with C_{60} up to the molar ratio $[ClO_2]_0$:$[C_{60}]_0 = 60$:1. As the $[ClO_2]_0$:$[C_{60}]_0$ ratio was further increased, unreacted chlorine dioxide could be detected in solution by EPR and UV-VIS spectroscopy. Thus, up to 60 molecules of ClO_2 were consumed by one fullerene molecule. In the presence of even very small amounts of ethanol (*ca.* 1%), neither the precipitate formation nor the EPR signal were observed. Furthermore, the addition of ethanol to the precipitate led to a decrease in the EPR signal intensity. Two new bands at 900–1400 (br.) and 1732 cm^{-1} appeared in the IR spectra (KBr) of the precipitate obtained at the ratio $[ClO_2]_0$:$[C_{60}]_0 = 20$:1, whereas the characteristic bands of the fullerene at 528, 578, 1180 and 1428 cm^{-1} disappeared.

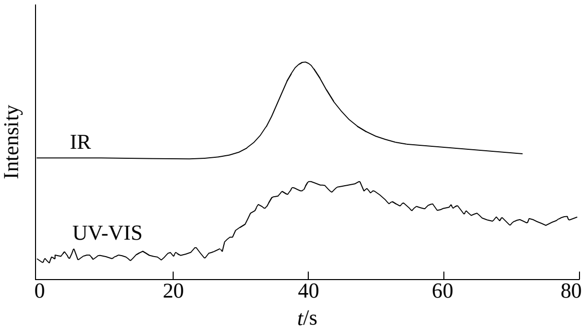

Figure 1 IR and visible chemiluminescence during the ClO_2–C_{60} reaction ($[C_{60}] = 1.4\times10^{-3}$ M, $[ClO_2] = 2.5\times10^{-2}$ M, benzene solution, 25 °C).

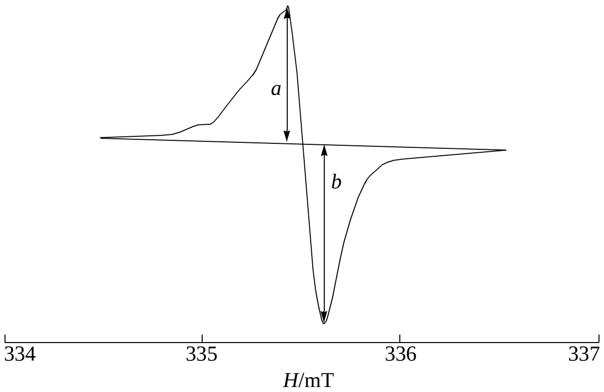

Figure 2 EPR spectrum of the precipitate obtained at the ratio $[ClO_2]_0/[C_{60}]_0 = 20$:1.

We attributed this EPR signal to a radical cation of the fullerene or its derivative. Parameters of the signal are similar to those reported for $C_{60}^{\cdot +}$ ($g = 2.0024$, $\Delta H_{pp} = 0.08$–0.13 mT), the ΔH_{pp} value and the intensity weakly depend on temperature.[8] Disappearance of the signal with the addition of ethanol testifies in favour of the radical cation nature of the signal, because it has been shown previously that alcohols readily react with $C_{60}^{\cdot +}$.[8] An induction period and high stoichiometry indicate that a multi-step process occurs in this system; apparently, chain decomposition of ClO_2 takes place. The chemiluminescence during the reaction is also indicative of the complex character of this process. The origin of this chemiluminescence and its possible emitters are unclear at this time. The oxidation potential of the fullerene ($C_{60}^{\cdot +}/C_{60}$) is substantially higher than the reduction potential of chlorine dioxide (ClO_2/ClO_2^-). Thus, direct oxidation of the fullerene is highly improbable. The first step of the reaction can be the formation of a product of covalent addition of ClO_2 to the fullerene, and its further oxidation by chlorine dioxide can lead to the radical cation. During the chain reaction, the formation of much stronger oxidants (*e.g.*, ClO) is also possible. These oxidants can further react with C_{60} to form the radical cation. The latter can undergo the Friedel–Crafts type addition to an aromatic solvent (benzene or toluene) to give phenyl-substituted fullerenes.[8]

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