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Photo-, radio- and sonostoragechemiluminescence of buckminsterfullerene C_{60}

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Abstract

Buckminsterfullerene, C_{60}, exhibits photo-, radio- and sonostoragechemiluminescence. Photolysis, radiolysis or sonolysis results in stable products, while subsequent oxidation of the reaction mixtures, constitutes the chemiluminescence step. Besides being an energy storage system in the sense that light, ionizing radiation or ultrasound is absorbed, stored and light is emitted at will, the radiostoragechemiluminescence of C_{60} of the present work has the prospects of forming the basis of novel radiation dosemeters up to 500 Gy. Also, novel analytical applications for said fullerenes based on the photo-, radio- or sonostoragechemiluminescence promise detection limits as low as 7.2 ppb of sample. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Chemiluminescence; Photolysis; Radiolysis; Sonolysis; Fullerene

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1. Introduction

Since the discovery of buckminsterfullerene [1] and of new methods for large scale fullerene production [2] a huge amount of literature has been accumulated on the theoretical, chemical and physicochemical properties as well as applications of this intriguing species [3–12]. Despite the controversy on fullerene fluorescence, fullerene chemiluminescence (CL)-production of electronically excited products endowed with the exothermicity of a chemical reaction and subsequent emission of light has been reported [13–15]. We now wish to report the photo-, radio- and sonostoragechemiluminescence (PSCL, RSCL and SSCL) — terms that we have coined together to describe a complex phenomenon [16–20] where photolysis, radiolysis or sonolysis lead to stable products capable of chemiluminescencing [21] after suitable triggering of fullerene C_{60} in amide solvents on reaction with bases or Fenton's reagent (hydrogen peroxide/ferrous sulphate) and it should be noted here, that such systems can be considered as energy storage systems in the sense that light, ionizing radiation or ultrasound is absorbed and light is emitted at will, while there are good prospects for radiation dosimeters and novel analytical applications (Scheme 1).

2. Experimental techniques

2.1. Reagents

Buckminsterfullerene, C_{60} (99.9%), *N*,*N*-dimethylformamide (HPLC grade) (DMF) and ferrous sulphate hydrate × $7H_2O$ were purchased from Aldrich and used without further purification. Hydrogen peroxide was purchased from Panreac, Spain, as 30% water solution and diluted to 10^{-3} M. Working solutions were freshly made.

2.2. Equipment

Absorption spectra were run on a JASCO V-560 spectrophotometer and emission spectra on a JASCO FP-777 spectrofluorimeter (200 nm min^{-1}, emission band 5 nm). Chemiluminescence spectra could not be obtained because the CL intensity-time diagrams were narrow peaks. Infrared spectra were recorded with the aid of a Nicolet, Magna-IR spectrometer 550. Mass spectra (70 eV) (Micromass, Platform II, quadrupole) were recorded on a Labware instrument. NMR spectra were recorded in a Brucker AC 250 spectrometer.

2.3. γ-Radiolysis/photolysis/sonolysis

Photolysis was performed in a quartz cell (5 ml) with the full spectrum of a 1000 W xenon lamp in an Oriel

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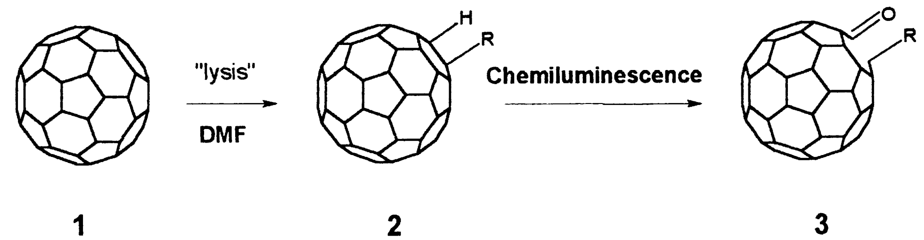


Scheme 1. Proposed reaction sequence for PSCL, RSCL and SSCL of fullerene C_{60} in DMF.

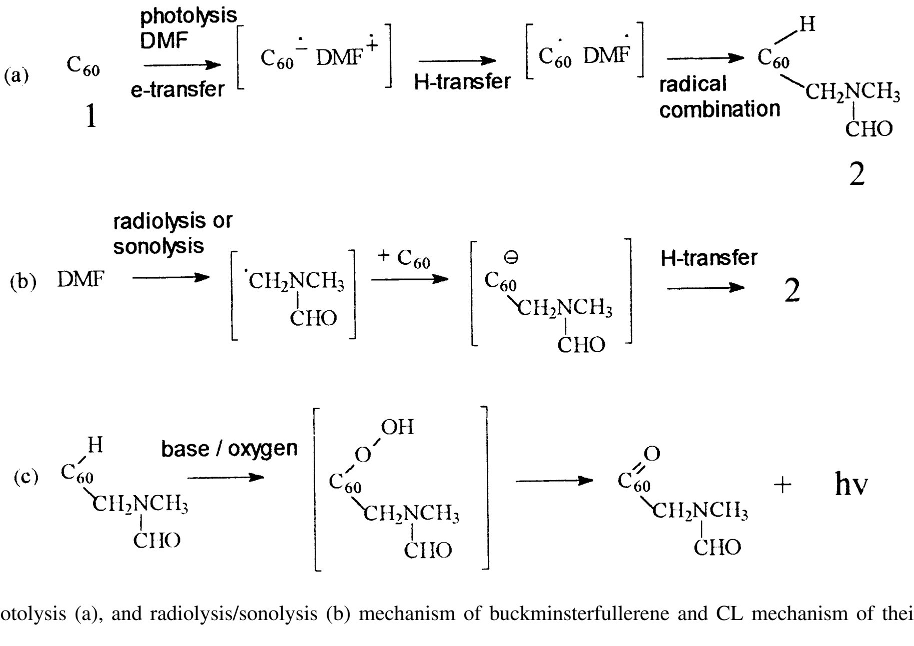
photolysis apparatus at room temperature; photolysis time 2 min. γ-Radiolysis experiments were performed in 10 ml conical flasks in a ^{60}Co source, 6500 Ci, Gamma Chamber (4000 A, Isotope Group, Bhaba Atomic Research Centre, Trombay, India). The dose rate was determined with Fricke's dosemeter [22] and was found equal to 24 Gy min^{-1}; radiolysis time 20 min. Sonolysis was performed in a Sultan 300, Pro-Sonic, 47 kHz sonicator bath; sonolysis time 180 min. Photolysis, radiolysis and sonolysis were considered complete on disappearance of the characteristic absorption band at 333 nm which occurred at the times indicated above (concentration of working solutions 1.38×10^{-5} M in DMF). When, however, a better solvent (DMF/dichlorobenzene) was employed resulting in much higher concentrations (9.1×10^{-4}), longer lysis times were required for the 333 nm band to disappear.

2.4. Chemiluminescence measurements

Chemluminescence measurements were obtained on addition of solid sodium hydride or methanolic potassium hydroxide solutions (250 μl, 1.5 M) or Fenton's reagent (ferrous sulphate 250 μl, 10^{-3} M, and hydrogen peroxide 250 μl, 10^{-3} M) into oxygenated solutions of the photo-, or radio- or sonolyzed fullerene C_{60} (500 μl, 1.38×10^{-5} M) in the dark chamber of a 1250 Bio-Orbit luminescence photometer with the timer circuitry disconnected. The cell's jacket was thermostatically controlled with the aid of a constant temperature bath-circulator and the temperature was maintained at 25°C. Temperature control was unnecessary, however, as there was no difference in lysis and CL at other temperatures around RT. The light intensity-time integrals thus obtained were compared with the luminol standard [23] which served as an absolute photon source under the same geometry. The quantum yields based on fullerene C_{60} employed before illumination, irradiation or sonication were in the order of 10^{-6} einstein mol^{-1}. The duration of light emission was not longer than few seconds.

2.5. Product identification

All efforts to isolate the photolysis, radiolysis or sonolysis products were fruitless although the products were stable in solution at room temperature. The UV and fluorescence spectra did not change after few days and the same is true for the CL profiles and efficiencies. Absorption, fluorescence



Scheme 2. Proposed photolysis (a), and radiolysis/sonolysis (b) mechanism of buckminsterfullerene and CL mechanism of their "lyzed" products (c).

and NMR spectra in DMF solution indicated similar addition products to the fullerene rings. The one and only signal in the ^{13}C NMR spectrum ($CS_2/CHCl_3$) due to the symmetric initial fullerene at 140 ppm, is replaced in the photolysis, radiolysis or sonolysis spent reaction mixture by a number of signals in the region between 140 and 125 ppm together with several others between 65 and 50 ppm indicating addition onto fullerene of groups from the decomposition of *N*,*N*-dimethylformamide, with basic fragment dimethylformamide itself ($CH_2N(CH_3)CHO$). Such a structure (**2**, Scheme 2) was verified by its synthesis photochemically, following the method of Siedschlag et al. [24] and comparison of its absorption and fluorescence spectra with those of the photolysis, radiolysis and sonolysis spent reaction mixtures. Indeed, in contrast to fullerene which is non-fluorescent, at least under the conditions of our measurements, the lysis products gave peaks at 470 and 517 nm and so did adduct **2**. Although attempts to isolate and characterize the products of the lysis step met with little success. Although it was possible to purify the lysis reaction mixtures from the DMF polymers formed during the lysis step, we were unable to isolate any pure product. A chemiluminescence product was, however, obtained in the case of photolyzed fullerene and subsequent CL, after column chromatography (silica gel, methanol) which separated it from the DMF polymeric material produced during the lysis step. The mass spectrum of this product showed peaks at *m*/*z* 809 and 810 which may be attributed to structure **3** produced on oxidation of a methine carbon atom of the fullerene ring to a keto-group (IR, 1680 cm^{-1}), with group $CH_2N(CH_3)CHO$ still attached to fullerene. Structure **3** is also supported by the ^{13}C NMR spectrum showing a number of signals in the aromatic region (140–125 ppm) together with signals characteristic of the DMF methyl- and aminomethyleno-groups (39 and 53 ppm). A signal is also present at 69.8 ppm probably due to the sp^3 carbon atom of the fullerene ring.

3. Results and discussion

Within the framework of photo- and radiostoragechemiluminescence we have earlier reported the radiolysis of azaaromatics, reactions leading to reduction, disproportionation or coupling, with the amides playing the role of solvents/reagents [16–19,21]. In these reactions the coupling product was always the major product.

The photo-, radio- and sonolyzed products of fullerene C_{60} although stable in DMF solution could not be isolated by all forms of chromatography. In any case, isolation of the lysis products is not a prerequisite for proceeding to the second step, CL. In the radio-, photo- or sonostoragechemiluminescence reactions of the present work the lysis products mixtures were employed as they were for the CL reaction and the quantum yields herein reported are those of the overall process, i.e. they are based on the fullerene employed before illumination, irradiation, or sonication. Regarding the photo-, radio- or sonoreduction of fullerene in DMF the fullerene radical anion may be produced from fullerene through electron transfer from DMF, the solvent/reagent. As amines or amides are particularly good electron donors to photoexcited molecules [25], it is reasonable to assume that following the electron and proton transfer from the solvent/reagent, reductive aminomethylation proceeds via radical combination as shown in Scheme 2. This interpretation is also supported by the type of hydrogen abstraction in the radiolysis or sonolysis of DMF in which the DMF radical seems to be the principal intermediate [26]. A differentiation is, however, expected between radiolysis/sonolysis and photolysis. In the former case (Scheme 2, part (b)), it is the amide free radical ($CH_2N(CH_3)CHO$) that reacts with fullerene, whereas in photolysis (Scheme 2, part (a)) it is the excited fullerene that reacts with the solvent/reagent. In any case, the major end product should be the same. The main reactions may then be written as shown in Scheme 2.

Addition of base in the presence of air to the lysis spent reaction mixtures of fullerene resulted in medium-weak CL and similar efficiencies were obtained with pure oxygen. The light intensities and CL efficiencies depended on the strength of the base employed and this is shown in Table 1, with best results obtained with sodium hydride probably due to more efficient decomposition of the intermediate peroxides. Observations as (a) oxygen is required for the CL step, (b) fulleren-ones are always the end products and (c) linear peroxide decomposition fullfills the energetic requirements for CL offer support to the mechanism of Scheme 2.

Regarding the CL spectroscopy, it is unfortunate that we were unable to obtain a meaningful spectrum due to the relatively low light intensities which did not allow the recording of a continuous spectrum, but mainly due to the intensity-time profiles in the form of short bursts of light. Attempts to obtain intensity-time diagrams at different emission wavelengths and plot the peaks versus wavelength

Table 1
Chemiluminescence intensities and quantum yields of photo-, radio- and sonolyzed fullerene C_{60} in DMF[a,b]

Reagent	Photo-, radio-, sonostoragechemiluminescence intensities (arbitrary units)	Photo-, radio-, sonostoragechemiluminescence quantum yields × 10^6 (einstein mol^{-1})
Fenton's reagent	220/70/47	1.2/0.5/0.4
Methanolic potassium hydroxide, 1.5 M	395/70/47	2.6/0.1/0.2
Sodium hydride	580/364/249	5.7/3.3/2.4

[a] Fullerene concentration, 1.38 × 10^{-5} M; photolysis time, 2 min; radiolysis time, 20 min; sonolysis time, 180 min.

[b] Further lysis, beyond the disappearance of the peak at 333 nm leads to lower signals and quantum yields due to further reaction of the lysis products.

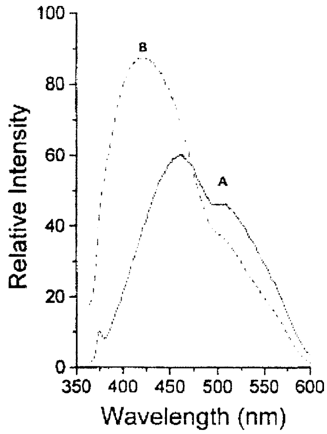


Fig. 1. Fluorescence spectra of (A) the reaction mixture after photolysis of deaerated fullerene C_{60} in DMF and (B) the reaction mixture after the CL step in the presence of air.

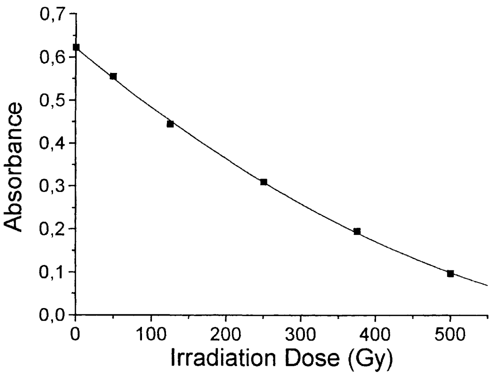


Fig. 3. Plots of the absorbance of fullerene C_{60} at 333 nm in DMF/*o*-dichlorobenzene solvent mixture (1:1) vs. absorbed dose from the ^{60}Co source; starting fullerene concentration, 9.1×10^{-4} M, followed by 1:10 dilution after radiolysis.

did not give a meaningful emission spectrum. The fluorescence spectrum, however, of the CL spent reaction mixture is usually a good approximation to the CL spectrum and this is shown in Fig. 1 together with that of the photolysis spent reaction mixture. In accordance with the mechanisms suggested above, the presence of oxygen is harmful during the lysis step (A); in such a case the ratio of peaks is reversed and the CL efficiency is appreciably lowered. Most probably the presence of oxygen in the lysis step leads to linear peroxides whose spontaneous decomposition leads to spontaneous CL and therefore lower efficiencies in the CL step. Conversely, oxygen is necessary for the CL step (B), and although, the concentrations of atmospheric oxygen may be negligible compared with DMF, the solvent/reagent, it is adequate compared with the photoproducts.

Besides being an energy storage system in the sense that ionizing radiation is absorbed, stored and light is emitted at will, the RSCL of C_{60} of the present work has the prospects of forming the basis of novel radiation dosemeters. As shown in Fig. 2, RSCL can be used as a radiation dosemeter from 50 to 500 Gy using 1.38×10^{-5} M fullerene solutions where the increase in CL intensity is well described by the linear equation: $y = A+Bx$, where y is the CL intensity and x the irradiation dose in Gy ($A = 1.26 \pm 0.5$; $B = 0.1318 \pm 0.002$, $r = 0.9995$, S.D. $= 0.753$, $N = 6$). It should also be noted that using UV spectroscopy the radiolysis step of fullerene can also be used for the determination of the irradiation dose as is shown in Fig. 3 on application of the polynomial equation $y = A + B_1x + B_2x^2$, where y is the absorbance and x the irradiation dose in Gy ($A = 0.622 \pm 0.005$, $B_1 = -0.00146 \pm 5 \times 10^{-5}$, $B_2 = 8 \times 10^{-7} \pm 1 \times 10^{-7}$, $r^2 = 0.9995$, S.D. $= 0.006$, $N = 5$). Also, novel analytical applications for said fullerenes based on the PSCL, RSCL, or SSCL promise detection limits as low as a few ppb of sample. As shown in Fig. 4, employing a higher fullerene concentration to expand the range of PSCL versus concentration PSCL can be employed in the determination of buckminsterfullerene in the region from 10^{-3} to 10^{-7} M where the increase in CL signals is well described by the polynomial equation: $y = A + B_1x + B_2x^2$ where y is the logarithm of CL inten-

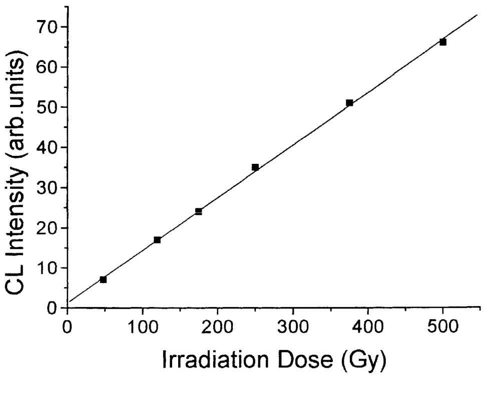


Fig. 2. Plots of the maximum CL intensity (luminometer) of fullerene C_{60} in DMF recorded in the intensity-time profiles vs. absorbed dose from the ^{60}Co source; starting fullerene concentration, 1.38×10^{-5} M, methanolic potassium hydroxide concentration, 1.5 M.

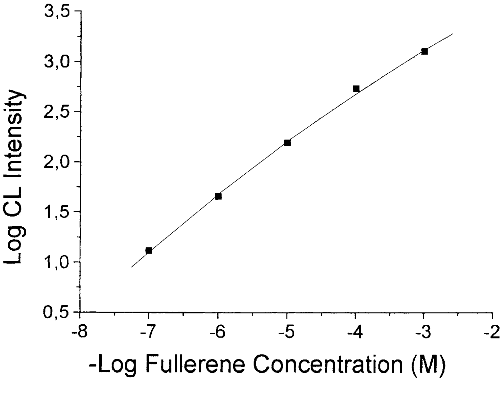


Fig. 4. CL Intensities vs. concentration of fullerene C_{60} in DMF/*o*-dichlorobenzene solvent mixture (1:1) after photolysis of a 9.1×10^{-4} M solution, dilution to the concentrations indicated and addition of the CL reagent.

sity and x the logarithm of fullerene concentration in $\mathrm{mol\,l^{-1}}$ ($A = 4.11 \pm 0.25$, $B_1 = 0.26 \pm 0.11$, $B_2 = -0.025 \pm 0.01$, $r^2 = 0.9987$, S.D. $= 0.039$, $N = 5$).

4. Conclusions

Despite the uncertainty in the photolysis, radiolysis and sonolysis as well as chemiluminescence mechanisms, photolyzed, radiolyzed or sonolyzed solutions of fullerene C_{60} in amide solvents are chemiluminescent. Besides being an energy storage system, the effect can be employed in radiaton dosimetry up to 500 Gy as well as in analytical applications for the determination of fullerene C_{60} down to 7.2 ppb ($72\,\mathrm{mg\,l^{-1}}$).

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