A New Method for the Preparation of Fullerene Anion Salts: Synthesis and Characterization of KC60(THF)

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Stoichiometric 1 : 1 reaction of C_{60} with potassium mediated by 1-methylnaphthalene in THF at room temperature produces KC_{60} (THF) in high yields; VIS–near IR, FTIR, solid-state ^{13}C NMR and ESR spectra of the product are reported.

The discovery of superconductivity in alkali metal fullerides (A_xC_{60}) has attracted considerable experimental and theoretical interest in the electronic properties of these and other fullerene anion salts.[1] In addition, fullerene anions are important synthetic precursors in the organic and organometallic chemistry of fullerenes.

The vapour-transport technique is widely used to produce phase-pure fulleride materials, such as KC_{60}, K_3C_{60}, K_4C_{60} and K_6C_{60}.[1a,2] This method, however, requires higher temperatures (200–400 °C) and longer reaction times (10–15 days). Alkali metal fullerides can also be obtained by reaction of C_{60} with alkali metal in liquid ammonia which requires lower temperature.[1a,3] Direct reactions of C_{60} with alkali metals in THF have been reported.[1a,4] Owing to the insolubility of both C_{60} and alkali metals, the reaction often requires higher temperature or long-time vigorous sonication. Stinchcombe et al. found that the addition of crown ether can overcome this problem partially, but in this case a large excess sodium were used.[5a] A novel solution phase route to $NaC_{60}(THF)_5$ was developed very recently.[5b]

We report here that alkali metal–naphthalene, a well-known powerful homogeneous reducing system in synthetic chemistry, can be introduced to prepare fullerene anions in THF at room temperature in an efficient and controlled way. This has been demonstrated by the synthesis and characterization of $KC_{60}(THF)$.

All manipulations were carried out under argon atmosphere with the rigid exclusion of air and moisture. To a suspension of C_{60} (240 mg, 0.33 mmol, >99.5% purity) in 50 ml THF were added potassium metal (13 mg, 0.33 mmol) and 1-methylnaphthalene (1–2 ml). The resulting mixture was stirred for 3 h (potassium metal and solid C_{60} disappeared completely within 2 h). After centrifugation (to remove possible trace impurities <5 mg), the black microcrystalline product was obtained by layering hexane over the dark red–purple solution. The solid was washed with hexane and dried in vacuum to produce KC_{60} (THF), (259 mg) in 94% yield. Elemental anal. $KC_{60}(THF)$, Calcd for $C_{64}H_8OK$: C, 92.42; H. 0.96. Found: C, 85.76; H, 1.09.

The relatively lower carbon data may arise from incomplete combustion of these high carbon content species.[5a] According to ^{13}C NMR (in [$^2H_8$]THF) and IR spectra (KBr), the product was not contaminated by 1-methylnaphthalene and hexane.

Compared with C_{60}, $KC_{60}(THF)$ shows intense and characteristic absorption bands in the VIS–near IR region (Fig. 1). Absorption at 1.075 μm (9300 cm^{-1}) for KC_{60} (THF) can be assigned to the allowed HOMO–LUMO $t_{1u} \rightarrow t_{1g}$ transition of C_{60}^- [4b,5a,6].

Room temperature solid-state ^{13}C NMR spectrum of $KC_{60}(THF)$ are shown in Fig. 2. A single peak with δ 187 is observed at 295 K and spin–lattice relaxation time T_1 is 15.9 ms. A downfield shift for fullerides has been reported previously.[1a,4a,5b] The narrowness of $KC_{60}(THF)$ signal (line width 16.2 ppm) suggests that C_{60}^- ion rotates rapidly at room temperature, thus averaging out the ^{13}C chemical shift anisotropy (CSA). No C_{60} signal is observed in our ^{13}C NMR spectrum. This indicates that disproportionation reactions such as $2\ C_{60}^- \rightarrow C_{60} + C_{60}^{2-}$ or $3\ C_{60}^- \rightarrow 2\ C_{60} + C_{60}^{3-}$ did not occur when the product was precipitating from solution. The C_{60}^- signal is strongly temperature-dependent. The chemical shift and linewidth of C_{60}^- increases with temperature decreasing (e.g. T 150 K, δ 208, line width 99 ppm), (although IR spectrum (KBr) indicated the apparent existence of THF in samples, no THF signals were detected in our ^{13}C NMR spectrum, which might be due to CSA).
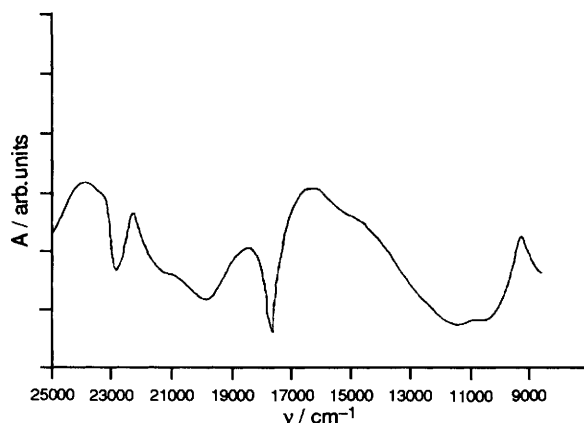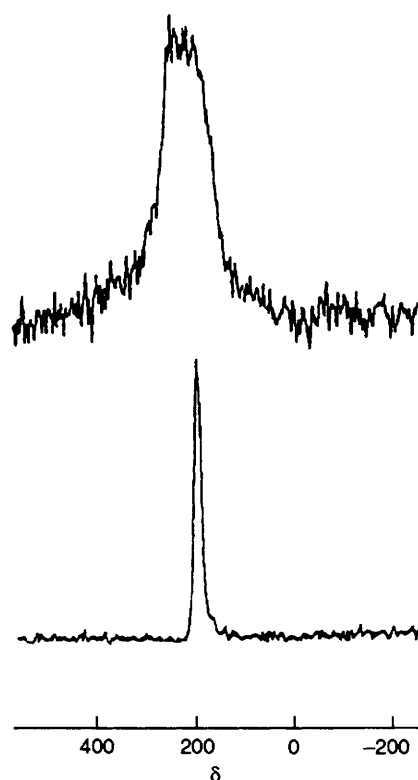

Fig. 1 VIS–near IR spectrum of $KC_{60}(THF)$ (solid sample in paraffin oil, recorded on Nicolet 800 FTIR spectrometer)

Fig. 2 Solid state ^{13}C NMR spectra of $KC_{60}(THF)$ (75.5 MHz, without sample spinning) [upper trace at 150 K, lower at 295 K]

In the region 400–600 cm^{-1} of IR spectrum (paraffin oil, Fig. 3), C_{60}^- exhibits two bands (575, 527 cm^{-1}) resembling that of C_{60} (577, 527 cm^{-1}), but with reversed ratio of relative intensities. This feature is in agreement with the charged-
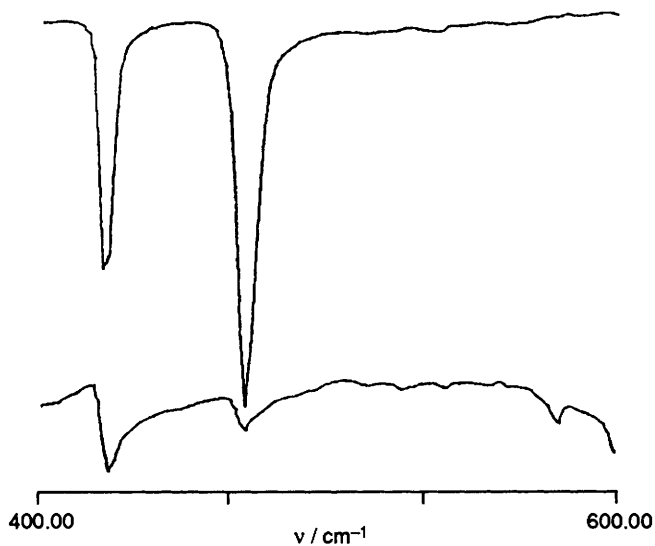

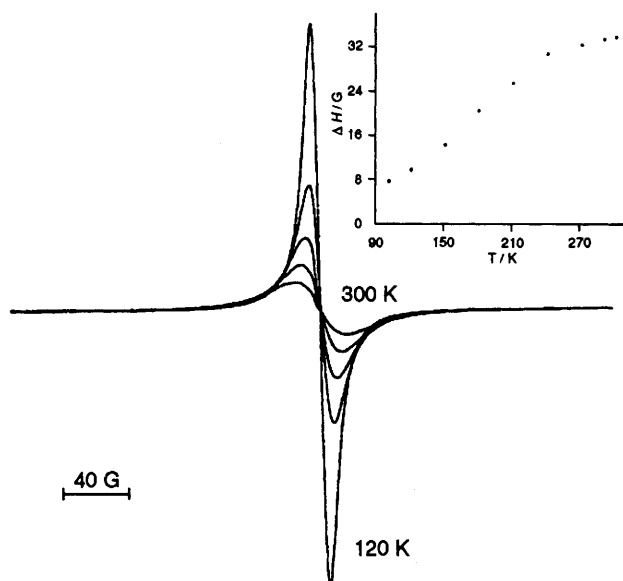**Fig. 3** FTIR spectrum (400–600 cm^{-1}) of C_{60} [above], KC_{60}(THF) [below]

Fig. 4 ESR spectra of KC_{60}(THF) as a function of temperature. Inset is change in line width with temperature.

phonon theory presented by Rice and Choi.[7] (An additonal band around 419 cm^{-1}, which is not due to paraffin oil, THF, hexane or 1-methynaphthalene, may be assigned to M–R mode, M=K$^+$, R=THF or C_{60}^-).

A single, broad ESR signal (g 1.9987, ΔH = 34.1 G) is observed for KC_{60}(THF) solid at 300 K (Fig. 4). The g value and temperature dependence of the signal line-width resemble those of C_{60}^- samples reported previously.[1c,5b,8] According to Stinchcombe et al.[5a] and our experimental results,[9] this can be assigned to ^2E state of C_{60}^-, which originates from the splitting of $^2T_{1u}$ state induced by Jahn–Teller distortion.

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