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Facile Sonochemical Synthesis of Graphite Intercalation Compounds

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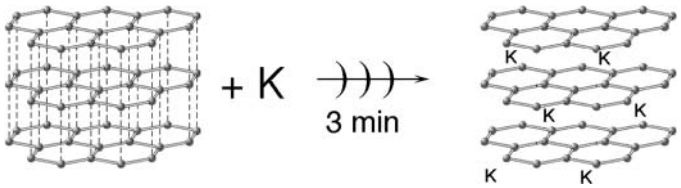
ABSTRACT



Graphite intercalation compounds (GICs) are useful as powerful reducing agents in organic chemistry and are typically prepared by anaerobic solid-state reactions at high temperatures for 1–8 h. We have been able to prepare KC_8 in situ in toluene using ultrasound *in less than 5 min*. This allows for a convenient approach to reductive chemical syntheses involving GICs.

The graphite crystal structure consists of stacked, two-dimensional sheets of carbon. Graphite intercalation compounds (GICs) are formed when alkali metal atoms are inserted into the spaces between the graphene planes. GICs are used as powerful and wide-ranging reducing agents[1−3] and/or polymerization catalysts in chemical reactions.[4,5] GICs have found recent application in the preparation of organometallic compounds,[6] phosphorus β-diketiminates,[7] Fischer carbenes,[8] amido and imido complexes,[9] and silylenes,[10] polysilylenes,[11] and polysilynes.[5,12]

A prototypical GIC is KC_8 (potassium-graphite), which is usually produced by heating a mixture of potassium metal and graphite in a solid-state reaction at elevated temperatures (150−200 °C) with vigorous stirring for 1 to 8 h in an inert atmosphere.[1] Alternatively, the potassium and graphite mixture can be heated under pressure.[13] A previously reported liquid-phase approach to the synthesis of KC_8 involves the use of a cobalt(0) catalyst in pentane at room temperature.[14] However, this reaction requires 1 or 2 days.[14,15] The formation of KC_8 is apparent from the development of a golden-bronze metallic coloration due to the delocalization of potassium 4s electrons into the graphite conduction band.[16]

We have developed a new process for the heterogeneous solid−liquid-phase preparation of KC_8 that is much faster than previous procedures and requires no external heating

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or pressure. In a typical reaction, stoichiometric amounts of potassium (0.5 g (12.8 mmol)) and graphite (1.229 g (102.4 mmol, which has been previously heated and degassed to remove adsorbed oxygen and water)) are added to a sonication cell[17] containing 15 mL of toluene that has been purged with argon for 45 min. The mixture is then subjected to high-intensity ultrasound under argon at room temperature using a Sonics and Materials 500W Vibra-Cell sonicator operating at 20 kHz with an acoustic power density of 17W/cm^2 as measured calorimetrically.[18] The intercalation process is largely complete after only 3 min of sonication. Similar intercalation of layered inorganic solids has been previously observed using high-intensity ultrasound as the energy source.[19] No GIC formation is observed using an ultrasonic cleaning bath even after several hours of sonication, indicating the profound difference in reactivity that can result when using a power ultrasound probe compared to low-intensity ultrasound.

The golden-bronze color of the graphite intercalation compound formed sonochemically in toluene is shown in Figure 1. This color is produced after less than 3 min of sonication, so long as the graphite has been heated to remove adsorbed oxygen.

Figure 1. Sonochemically prepared KC_8.

The XRD powder diffraction spectrum for a sample of potassium and graphite sonicated for 2 min in toluene is shown in Figure 2. We have been able to match the majority of the peaks in the XRD pattern with a KC_8 standard and with KC_8 produced by thermal means (see Table 1).

Sonication for a longer period of time produces a blue-black material, which may either be due to partial deintercalation or to the destruction of the intercalated material to reform graphite and potassium. After approximately 10 min of sonication, compounds with smaller K/C ratios are noticeably evident in addition to KC_8.

A stage 1 GIC such as KC_8 is formed if all the spaces between the carbon planes are occupied, while a stage 2 GIC corresponds to the case in which the spaces between every other carbon plane is occupied (KC_{24}).[20] After 1 h of sonication, the X-ray diffraction pattern shows evidence of stage 1 to stage 7 deintercalation. Graphite is also observed, due to complete deintercalation, along with the possible intercalation of toluene into the graphite layers. Table 2 lists the XRD peaks observed after 1 h of sonication, together with their tentative assignments.

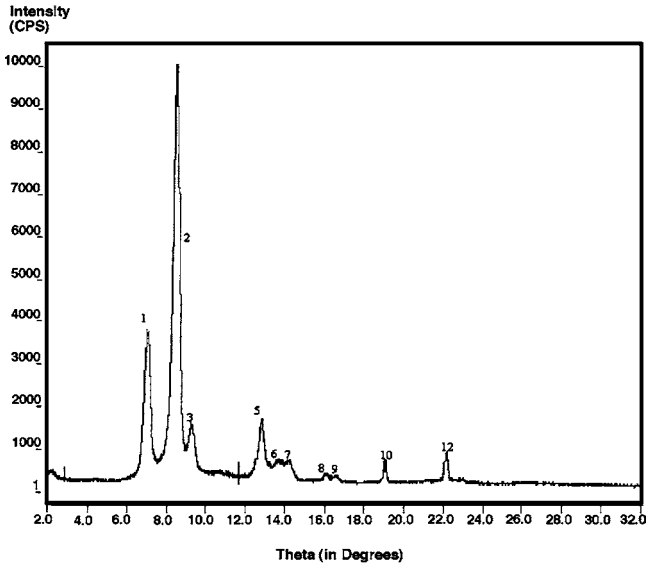

Figure 2. XRD spectrum of sonochemically prepared KC_8.

It has been previously reported that preparation of GICs in tetrahydrofuran results in the formation of ternary species in which some solvent molecules are intercalated into the graphite. Benzene and toluene can also be intercalated thermally.[1] We have not observed the sonochemical formation of KC_8 in either THF or hexane, even after 1 h of

Table 1. *d* (in Å) Space Value Analysis Using a Mo Kα Source for the Sonochemical Production of KC_8

sample *d* spacing	relative intensity	thermally prepared[a]	standard[b]	*hkl* (KC_8)
6.47	32	6.47		
5.35	100	5.35	5.35	004
4.88	6	4.88		
4.24	3		4.20	101
3.52	13	3.51	3.67	103
3.18	2	3.18		
		2.98	3.03	
2.82	1	2.82		003
2.72	1	2.73	2.67	002
			2.49	
2.38	3	2.39	2.41	112
2.06	4	2.06	2.04	116, 202
				204, 206

[a] Sample prepared by heating potassium and graphite at 150 °C for 1 h. [b] Standard for KC_8 provided by the powder diffraction file (d4-0224) compiled under the Joint Committee on Chemical Analysis by powder diffraction methods.

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Table 2. *d* Space Value Analysis (in Å) Using a Mo Kα Source for the Material Resulting from 1 h of Sonication of Potassium and Graphite in Toluene[a]

sample *d* spacing (Å)	relative intensity	proposed deintercalation material (*hkl*)
10.03	1	3s (001) or graphite (106)
6.27*	34	2s (001) or graphite (103)
5.23*	100	1s (001) (toluene?)
4.77*	7	2s (002)
3.47*	8	5s (005)
3.36	6	graphite (002)
3.14	1	7s (008)
2.86	1	2s (003)
2.68*	2	1s (002) or 5s (007)
2.35*	3	4s (007)
2.17	1	graphite (100)
2.13	1	graphite (001)
2.04*	7	graphite (101)
1.98	1	4s (008)
1.73	1	KC_{16} (206)
1.69	1	graphite (004)

[a] 1s = KC_8, 2s = stage 2, 3s = stage 3, 4s = stage 4, 5s = stage 5, 6s = stage 6, 7s = stage 7.[12]

sonication. The possibility exists that an aromatic solvent is necessary for interplanar expansion or intercalation prior to the addition of potassium to the lattice.

The KC_8 produced after 3 min of sonication can be used in quiescent reactions in the same manner as the thermally prepared material. Although deintercalation begins after a few minutes, the KC_8 and other deintercalation materials produced can still be used for subsequent in situ reactions, allowing for one-pot syntheses. We have used the sonochemically produced KC_8, for example, in the subsequent sonochemical preparation of polysilyne materials.[21] This approach should be generally applicable to the synthesis of a wide variety of graphite intercalation compounds.

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