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$C(CN)_5^-$: transition state or intermediate?

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Cyanide reacts with tetracyanomethane towards the tricyanomethyl anion *via* cyanophilic substitution; this is suggested by nitrogen isotope-labeling experiments and proven by density functional calculations at OLYP/TZ2P.

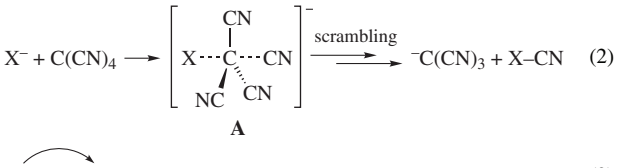
While cyanogen is considered a pseudohalogen, its organic derivatives, namely, nitriles, have almost nothing in common with corresponding alkyl/aryl-halogens. However, the accumulation of C≡N groups in a molecule may drastically change its effective properties and, in particular, increase the pseudohalogenic character. A review of the chemistry of polycyano compounds (*e.g.*, refs. 1, 2) easily reveals the unusual behaviour of such compounds. For example, pentacyanocyclopentadiene is a stronger acid than $HClO_4$,[1,2] tetracyanoquinone can oxidize water[1,2] and $C(CN)_4$ is extremely reactive and is a good cyanating reagent, as compared with $C(Halogen)_4$.[2,3] The latter is illustrated by the reactions of $C(CN)_4$ with inorganic salts, which easily proceed in accordance with the following scheme:[1,2(*d*),3(*c*),4,†]

$$C(CN)_4 + MX \longrightarrow MC(CN)_3 + X\text{–}CN, \quad (1)$$

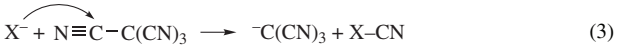
where M = Li, Na, K; X = F, Cl, Br, CN.

Another interesting consequence of the accumulation of C≡N groups around a carbon atom, first shown by R. Hoffmann *et al.*,[5] is a significantly reduced energy demand associated with the transformation from a tetrahedral into a planar $C(CN)_4$ configuration if compared to a 'normal' tetra-coordinate carbon as, for example, in methane. This theoretical result permits one to think about possible unusual geometries of polycyano compounds (*cf.* selected examples of the search on unusual geometries and bonding of carbon[5,6]).

Consider the possible mechanisms for the process shown in equation (1). One may suggest two possible pathways:[1] a nucleophilic attack at the central carbon atom [equation (2)] *via* transition state/intermediate **A** or 'cyanophilic' attack at the *sp*-hybridized carbon of a C≡N group [equation (3)]:[7]



(2)



(3)

The crucial point in the case of the mechanism in equation (2) is whether **A** is an intermediate or not, especially for the symmetrical case when X = CN and thus **A** corresponds to D_{3h} symmetric $C(CN)_5^-$. In an attempt to answer this question, we have performed reaction (1) with MX being labeled $K^{14}CN$. The idea was the following: if $C(CN)_5^-$ is a reactive intermediate and it can undergo Berry pseudorotation, one may observe a scrambling of the ^{14}C label. The experiments resulted in the exclusive isolation of unlabelled $KC(CN)_3$ with low yield.‡ This experiment is not very informative (because the analytical problem of detecting all reaction components have not been entirely solved), but anyhow it is in agreement that $C(CN)_5^-$ is probably a transition state. Yet, reactive intermediate **A** cannot be ruled out entirely on the basis of these observations.

To obtain further evidence on the active reaction mechanism and the nature of $C(CN)_5^-$, we have conducted a theoretical investigation at the OLYP/TZ2P level as implemented in the Amsterdam Density Functional (ADF) program.[8] Recently, it was shown that the reason for carbon's inability to form stable pentavalent $[R\text{–}CR'_3\text{–}R]^-$ species is its size, *cf.* the ball-in-a-box (BiaB) model.[9] Thus, the five substituents can be conceived as a box, $[R\text{–}R'_3\text{–}R]^-$, in which they are in steric contact. The central C atom is then too small to achieve its intrinsic optimal C–R bond distance simultaneously with both axial substituents R (at variance, the larger Si atom does fit into such a box and, therefore, forms stable pentavalent $[R\text{–}SiR'_3\text{–}R]^-$ species). However, it was also shown that stable pentavalent carbon species can be formed if the central CR'_3 disk is sufficiently rigid to oppose to pyramidalization, *cf.* the disk-between-balls (DbB) model.[10] In this way, stable anionic pentavalent carbon could be identified for the first time computationally in the series of $[X\text{–}C(CN)_3\text{–}X]^-$ with X one of the heavier halogens, I or At.[11]

In line with the BiaB and DbB models, the propensity of $[X\text{–}C(CN)_3\text{–}X]^-$ to adopt a stable D_{3h} symmetric equilibrium structure increases as the proton affinity (PA) decreases along $X^- = F^-$, Cl^-, Br^-, I^- and At^-; the corresponding PA values are 1561, 1398, 1356, 1322 and 1314 kJ mol^{-1}, respectively, computed at BP86/TZ2P.[12] Thus, according to these models, the present $C(CN)_5^-$ species, *i.e.*, $[X\text{–}C(CN)_3\text{–}X]^-$ with X = CN, should not be a stable D_{3h}-symmetric equilibrium structure because the cyanide PA value[13] of 1469 kJ mol^{-1} is in between those of fluoride and chloride, which both lead to labile $[X\text{–}C(CN)_3\text{–}X]^-$ transition states for S_N2 substitution.

† The formation of cyanogen has not been experimentally detected (*cf.* ref. 4).

‡ Carefully ground 50 mg of $K^{14}CN$ and 0.6 g of carefully ground $C(CN)_4$ were placed under N_2 into a test-tube and heavily shaken during 24 h at room temperature under light vacuum. Then, 0.1 g of $C(CN)_4$ and 2 ml of acetonitrile were added to the solid, the mixture was shaken for another 24 h and all volatiles were carefully eliminated in a high vacuum. The residue was washed by acetonitrile, benzene and diethyl ether. Identification[3] of the solid revealed formation of potassium tricyanomethide (~30% yield) having no extra radioactivity.

Indeed, an exploration of the potential energy surface (PES) of the model reaction system $CN^- + C(CN)_4$ reveals that nucleophile attack by cyanide at the central carbon of tetracyanomethane proceeds *via* a D_{3h}-symmetric transition state (imaginary frequency = i471 cm^{-1}) at –28.3 kJ mol^{-1} relative to reactants (see Table S1 in the Online Supplementary Materials). Thus, **A** is not a reactive intermediate. The exploration of the PES furthermore shows that there is no stable reactant complex and the cyanophilic attack [equation (3)] proceeds without a barrier toward a product complex [NCCN, $^-C(CN)_3$], which is bound by 14.4 kJ mol^{-1}. The overall reaction towards the highly stabilized tricyanomethyl anion is rather exothermic, namely, by 341 kJ mol^{-1}.

In conclusion, our calculations show that $C(CN)_5^-$ is not a stable intermediate but a transition state and that the reaction of $^{14}CN^- + C(CN)_4$ leads to $C(CN)_3^- + NC^{14}CN$ *via* cyanophilic substitution, without isotope scrambling. This is in line with our experimental observations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.03.002.

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