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THE POTASSIUM METAL REDUCTION OF PERYLENE IN TETRAHYDROFURAN: EVIDENCE FOR THE PERYLENE DIANION

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Abstract. Reduction of perylene with potassium metal in tetrahydrofuran at room temperature yields the dianion, as determined by potassium metal uptake, by ^{1}H NMR of the anion solution, and by product analysis of a methyl iodide quench. There is no evidence for decomposition of the solvent, either to a butoxy fragment or to an ethylene/enolate mixture, a result which is in contrast to previously reported work on the naphthalene/alkali metal/tetrahydrofuran systems.

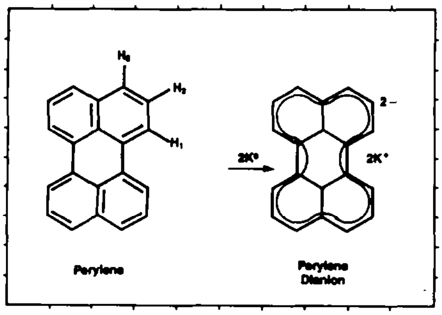
1. **INTRODUCTION.** In the last four years, there has been considerable discussion about the possibility of formation of tetraanions of both pyrene and perylene by reduction with alkali metals in tetrahydrofuran at room temperature.[1-6] This discussion has yielded insights into π-charge distribution in anions of aromatic hydrocarbons, correlations between charge distribution and chemical shifts in nuclear magnetic resonance, effects of pairing between aromatic ions and alkali metal cations, and solvent stability in strongly reducing systems.

Overlooked in this fundamental discussion has been the extension of these concepts to other benzenoid systems, including such diverse species as graphite and fossil fuels. Herein, we present new findings on the perylene/tetrahydrofuran/potassium system, and we discuss their relevance to work on the pyrene system of Schnieders, Mullen, and Huber (SMH)[5] and to work in other benzenoid systems.

2. **RESULTS.** As with SMH, we were intrigued with the possible existence of "super-charged" anions of relatively small aromatic hydrocarbons. While they and others investigated the case of pyrene,[4-6] we studied the case of perylene. Reduction of perylene with K° at room temperature yields the dianion of perylene after 7 to 14 days of reaction. This is determined by monitoring the weight of potassium consumed, by measurement of the ^{1}H NMR of the dianion in a sealed tube, and by determination of the products of a quench with CD_3I.

2.1 **NMR of Perylene Reduced by Potassium in Tetrahydrofuran at Room Temperature.** In a reaction involving perylene in [$^2D_8$]-tetrahydrofuran (.048 mmol perylene/g, THF) at 23°C in a He-filled box, samples were removed at varying intervals, sealed in 5 mm NMR tubes, and investigated for proton NMR at 400 MHz. After 1 month 2 weeks of reaction, we obtained a pattern with only 3 sets of resonances in the 4 - 9 δ region: a doublet of doublets (3 lines resolved) centered at 5.89 δ (J=7.8 Hz, 6.8 Hz), a doublet at 4.95 δ (J=7.8 Hz), and a doublet at 4.85 δ (J=6.9 Hz). The integrated intensities were in the range 1:1:1. A second reaction was performed (0.051 mmol perylene/g, THF), and after 9 days one observed both major peaks at 5.87, 4.94, and 4.83 δ (with no resolved spin-spin coupling) and less intense peaks at 7.15, 6.33, 5.56, and 5.41 δ. The intensity of the three main peaks, referenced to the claimed isotopic purity of the tetrahydrofuran, indicated that 50% of the protons of the perylene were represented in the three peaks. In all spectra, paraffinic resonances near 1.26 and 0.88 δ were observed, and these can be matched to a spectrum of the mineral oil used to protect the potassium metal.

Our observation of three resonances for the product of perylene with alkali metal is consistent with work reported by Lawler and Ristagno[7] in 1969 for the perylene dianion (4.99 δ, 5.93 δ, and 4.87 δ, with sodium metal) and with the work reported by Minsky, Meyer and Rabinovitz[2] in 1982 for the perylene tetraanion (4.91 δ (d), 5.86 δ (dd), and 5.02 δ (d), with sodium metal). As depicted in the figure, both perylene itself and anions derived from perylene would be expected to have three inequivalent proton environments. The resonance positions for perylene itself were reported by Lawler and Ristagno as 8.27 δ (H_1), 7.45 δ (H_2) and 7.70 δ (H_3).[7] The main point of our NMR results is that they are consistent with past reports, thereby establishing that we have performed



the same chemistry as the previous workers. The issue is whether such spectra correspond to the dianion or to the tetraanion of perylene.

2.2 **Reaction of Perylene Anions in Tetrahydrofuran with Methyl Iodide at 0°C.** In a separate reaction involving [$^1H_8$]-tetrahydrofuran, we found a ratio of 1.98 K° consumed per perylene after 9 days 6 hours of reaction at room temperature. At this time [$^2D_3$]-methyl iodide in tetrahydrofuran was syringed into the anion solution, and analysis performed by GC/MS. The most intense peak in gas chromatography showed the MS pattern of di-CD_3 di-H perylene (molecular ion at m/z = 288.2 (I=10.6), CD_3-loss ion at 270.2 (I = 100), di-CD_3-loss ion at 252.1 (I=99.4) and doubly charged ion at 126 (I=66.8)). This peak in the GC/FID amounted to 72% of the total identifiable perylene-derived molecules; perylene itself corresponded to 11%, a second isomer of di-methyl di-hydro perylene to 11%, with most of the balance corresponding to a tri-methyl di-hydroperylene, in which one methyl group replaces a hydrogen on the perylene (molecular ion at m/z = 305.2 (I = 19.3), CD_3-loss peak at 287.2 (I = 82.1), di-CD_3-loss peak at 269.2 (I = 100), no ion at 252, doubly-charged ion at 134.5 (I = 37.7)). It must be stressed that this tri-alkyl di-hydro perylene derivative contains one methyl group directly bound to an aromatic carbon, as is evident from the m/z ratio of the doubly-charged ion, 134.5 rather than 126. There is no evidence for tetra-methyl tetra-hydro perylene products (molecular ion at m/z = 324), as might be expected from the alkylation of the tetraanion of perylene. Furthermore, there is no evidence for perylene derivatives bearing fragments derived from decomposition of the solvent tetrahydrofuran.

To further seek these latter possibilities, we reduced perylene in tetrahydrofuran at room temperature withe excess potassium metal for a period of two months and two days. Again adding deuterated methyl iodide to the anion solution, we find one isomer of di-methyl di-hydro perylene to constitute 72.5% of the recovered perylene (MS: molecular ion at m/z = 288.2 (I = 16), CD_3-loss at 270.1 (I = 72), di-CD_3 loss at 252.1 (I = 100), doubly-charged ion at 126 (I = 40)). There is another di-methyl di-hydro perylene isomer of abundance 10.6%, a tri-methyl di-hydro perylene derivative of abundance 6.4%, a third di-methyl di-hydro perylene isomer of abundance 1.8%, and perylene itself of abundance 5.6%.

2.3 **Reaction of Perylene Anions in Tetrahydrofuran with Protic Sources.** To demonstrate the presence of tetraanions, Minsky, Meyer, and Rabinovitz reported the formation of tetradeuteriotetrahydroperylene (molecular ion at m/z = 260) following a quench with D_2O.[2] Using both forward and reverse quenches with D_2O, we do find such ions, but they correspond to GC peaks with the retention time of perylene itself. Since such a hydro-perylene species was recognized to be unstable,[2] we quenched a solution of perylene anions by addition of [$^2D_4$]-methanol at room temperature within a He-filled box, and we sealed the quenched solution in an NMR tube, just as with the anion solutions. Proton NMR at 400 MHz revealed a complex aromatic region with roughly six "packets" of resonances: 6.75 δ (d), 7.04 to 7.26 δ, 7.42 to 7.47 δ, 7.66 to 7.71 δ, 7.88 to 8.10 δ, and 8.20 to 8.25 δ. The packets beginning at 6.75 δ, 7.04 δ, and 7.88 δ could be associated with a molecule other than perylene. In terms of a possible di-deuterio di-hydro perylene derivative, we observed only a broad, weak peak near 6.18 δ and no signals whatsoever between 5 and 6 δ. In the aliphatic region, there were peaks near 2.0, 2.45, and 2.80 δ.

For reference, we ran at 60 MHz a sample of commercially available 1,2 di-hydro naphthalene; the olefinic proton at the 4 position comes at 6.35 δ and the olefinic proton at the 3 position at 5.88 δ. The methylene protons at the 1 position come between 2.45 and 2.80 δ, and the methylene protons at the 2 positions come between 1.80 and 2.30 δ.

3. **DISCUSSION.** In the reduction of perylene by potassium in tetrahydrofuran, both potassium consumption values and products of quenches with methyl iodide suggest the intermediacy of the dianion, rather than of the tetraanion, of perylene.

Analysis of products of quenches with protic sources suffers from the possible instability of the products to air and/or the analysis conditions themselves. Our NMR work on the perylene anion quenched by [$^2D_4$]-methanol suggests that di-deuterio di-hydro perylene was not formed. More probable is a disproportionation of said compound into tetra-deuterio tetra-hydro perylene and perylene itself. When an aliquot of this particular perylene anion solution was quenched by methyl iodide, di-methyl di-hydro perylene was the most abundant product, as we have found in our other reactions.

In the area of graphite/alkali metal chemistry, there has been considerable discussion about the magnitude of charge transferred from metal to graphite in the first stage compounds C_8M.[8-11] If the "super-charged" anions of pyrene and perylene existed, it would be facile to argue that inter-electron repulsions in the anion of the "infinite" graphite would have to be trivial in comparison to the tetraanions of small molecules as pyrene and perylene. In fact, SMH show that there is no tetraanion of pyrene, that even the dianion requires "prolonged metal contact", and that ion pairing and solvation effects are quite important in the dianion identity. Whereas our work with perylene indicates similar results, we suggest that the tetraanions of pyrene and perylene cannot be used to justify formulations for graphite/alkali metal intercalation compounds of the form $C_8^-K^+$.

In the case of fossil fuels, there has been much discussion about the detailed mechanism of the reductive alkylation chemistry proposed by Sternberg, an approach which imparts high levels of solubility to such refractory materials as coals.[12-15] Herein, the substrate (e.g., the coal) is combined with potassium, naphthalene, and tetrahydrofuran at room temperature, so that synthetic conditions are analogous to those used to make the anions of pyrene and perylene. Of course, coals contain a variety of sizes of aromatic hydrocarbons, and they contain heteroatoms including oxygen, nitrogen, and sulfur, so that their chemistry will be more complex than that of either pyrene of perylene.

There has been debate about the relative abundance of π-aromatic anions in comparison to anions derived from heteroatoms (e.g. phenoxides) following the reduction step in the reductive alkylation. Although electron spin resonance shows little evidence for aromatic radical anions[15], it has been argued much of the potassium goes to the formation of spin-paired dianions and presumably even tetraanions.[16] The work of SMH shows that tetraanions of benzenoid species are unlikely under Sternberg's conditions and that even dianions require considerable time for stoichiometric formation. Thus, even when one can, in principle, obtain dianions, one will see a strong ESR signal from the corresponding radical anion.

Another issue surrounding the reductive alkylation chemistry is the stability of the solvent system during the long reaction times required to effect reduction (ca. 4-7 days). Although much attention has focused on the possibility of the formation of C_4H_8O fragment[16], our work on naphthalene/alkali metal systems in tetrahydrofuran showed that such a fragment occurs with lithium but not with sodium or potassium,[17] a finding which is directly supported by the work of SMH. In the case of the naphthalene/potassium/tetrahydrofuran system, we have reported the formation of various mono-ethylated naphthalene derivatives, with the ethyl group coming from a cycloreversion of the solvent tetrahydrofuran.[17] This behavior is distinct from that reported by SMH for pyrene/sodium/THF and by us for perylene/potassium/THF, in which no such derivatives are found. Clearly, in assessing solvent stability, both the alkali metal and the aromatic substrate play a role.

Possible problems with solvent instability have led to the use of other reducing systems for fossil fuels, including alkali metal in tetrahydrofuran/ammonia.[14,16] The work of SMH serves to highlight distinctions in the reduction of aromatics with and without ammonia, most pointedly the capability of ammonia to serve as proton source during the reduction step. This work extends earlier insights of Rabideau and Burkholder.[18,19]

Of course, the main focus of the discussion about the possibility of tetraanions has been of a more fundamental nature, with much said about the nuclear magnetic resonance. As noted by SMH, electron exchange processes severely inhibit structural assignments. The anions of pyrene may be somewhat atypical in this respect, for the dianion shows broad lines at room temperature, unlike the previously reported dianions of anthracene, tetracene, acenaphthylene, fluoranthene, and perylene[7], with the perylene result corroborated by our work. A possible explanation for this linewidth behavior has been offered.[20] Finally, one notes slight discrepancies in the proton NMR shift values reported for the anion of perylene by the three separate sets of workers. The shifts of pure aromatic molecules can exhibit a concentration dependence because of the tendency of aromatic molecules to align in parallel in the solution state,[21] a phenomenon observed in the x-ray diffraction of aromatic liquids[22,23], so one must consider both intermolecular and intramolecular effects in analyzing the observed chemical shifts. With alkali metal counter-ions, different workers have reported even more varied results (compare the work of SMH to that reported by Cox, Terry and Harrison for the pyrene dianion with lithium[24]).

4. **EXPERIMENTAL DETAILS.** Perylene (Gold Label) was obtained from Aldrich, and potassium (reagent grade) was obtained from Alfa. The tetrahydrofuran was from Fisher, and was distilled from potassium benzophenone ketyl prior to use. Anion synthesis was accomplished by adding potassium metal to perylene in tetrahydrofuran, all contained within a VAC atmospheres glove box under helium[25]. A blue color developed on contact. One reaction in p_8-THF involved 1.961 g perylene, initially with 27 mL THF and 1.844 g K°; one reaction in d_8-THF involved 0.122 g perylene, 10.047 g d_8-THF, and 0.197 g K°. In a third reaction in p_8-THF, gravimetry showed K° consumption to be 2.01 K/perylene after 12 days 22 hours. Following methyl iodide quench, the mass of filtered, solid KI corresponded to 0.96 mole KI/mole K.

Our GC/MS analysis was carried out on a Hewlett-Packard 5995, equipped with two equal GC columns, one going to a quadrupole MS, one going to a flame ionization detector. An HP fast analysis column was used (part 19091A #101), which is 12.5 meter long (0.2mmID), with a cross-linked dimethyl silicone liquid phase. The temperature program employed a 6 min residence at 100°C, with a 15°C/min ramp to 276°C. The major di-methyl di-hydro perylene isomer eluted at 15.98 min, the minor at 16.38 min, the tri-methyl di-hydro perylene at 16.56 min, and perylene itself at 17.44 min.

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