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Nitration and sulfonation of polycyclic aromatic hydrocarbons under mild conditions yields derivatives with potent mutagenic and anti-bacterial properties

When benzene is treated with a mixture of concentrated nitric and sulfuric acid, it undergoes nitration by a process called "aromatic electrophilic substitution (AES)." Similarly, treatment with concentrated sulfuric acid alone results in sulfonation of the aromatic ring. Because it is a single-ring aromatic, benzene is a poor substrate for AES and thus requires rather harsh conditions for the reactions to occur. Polycyclic aromatic hydrocarbons (PAHs), on the other hand, having much larger pi-electron clouds (the target for the attacking electrophile), should be much more susceptible to AES. To test that hypothesis, a mixture of PAHs known as the "EU 15+1 PAHs" was treated with either concentrated nitric acid or sulfuric acid at room temperature (nitration) or 80º (sulfonation). Examination of the products of the former reaction by GC-MS revealed the presence of nitro-derivatives of three- and four-ring compounds, but not of the higher-molecular-weight species, which may have insufficient volatility to GC. No sulfono-derivatives were seen in the latter reaction mixture, although the parent compounds were largely absent from the chromatogram, indicating that reaction had occurred. From previous work, it was known that nitroaromatic compounds like 1-nitropyrene and 1,8-dinitropyrene are potent bacterial mutagens. Ames testing of the two sets of product compounds revealed that all except naphthalene were mutagens. Mutagenic potencies ranged over five orders of magnitude, the most potent derivative being nitrated pyrene, which produced approximately two million mutations per microgram, a number consistent with previous reports of 1,8-dinitropyrene having that level of Ames Test activity. The ease of synthesis of this little-studied group of compounds from readily available precursors has a number of implications, both chemical and biological. From the chemical standpoint – with or without further modification, such as reduction of the nitro-function – the compounds might make useful chemical intermediates and based on their strong polarity, potential surfactants. From the biological side, their extreme mutagenicity to bacteria, but much less so to mammalian cells, suggests that they could find use as industrial biocides, sewage sterilants and possibly even therapeutic agents for bacterially-mediated diseases.

Biography

Gary Blackburn is president of PetroLabs Inc., a testing and consulting firm serving the international petroleum industry. He holds a B.S. in chemistry from Wilkes University and a Ph.D. in oncology from McArdle Laboratory for Cancer Research at the University of Wisconsin. After doing postdoctoral research in the areas of radiation biology and chemical carcinogenesis, he joined Mobil Oil Corporation as a genetic toxicologist. While with Mobil, he and his colleagues developed the Modified Ames Test, the most widely used mutagenicity assay for petroleum materials. He is the author of more than 50 publications, most of which deal with the chemistry of polycyclic aromatic compounds as it relates to their mutagenic/carcinogenic potential.

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