Oxygen as a Reagent Gas for the Analysis of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin by Negative Ion Chemical Ionization Mass Spectrometry

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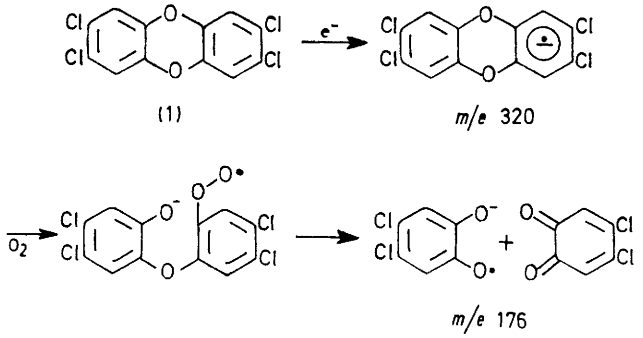
Summary Under negative ion chemical ionization conditions, the radical anion of tetrachlorodibenzo-*p*-dioxin (TCDD) undergoes a novel reaction with oxygen to produce an ion which is characteristic of structure and easily identified in the presence of other halogenocarbon contaminants.

In recent years herbicides, fungicides, and other preparations derived from polychlorinated phenols have been shown to contain 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (**1**) as a minor contaminant.[1] Since TCDD is lethal at the 1 part in 10^9 level and might exhibit sub-lethal toxicity at even the 1 part in 10^{12} level, analytical methods for detecting and estimating this compound must be sensitive at the picogram level. TCDD is analysed at present by the use of a high resolution mass spectrometer interfaced to a CAT and operated in the electron-impact mode.[2] Although the biological samples are subjected to extensive clean-up procedures, a repetitive scanning high-resolution analysis is required to maximize sensitivity and to eliminate interfering fragment ions from ubiquitous contaminants such as the pentachlorobiphenyls, DDT, and DDE which appear at the same nominal mass as the molecular ion from TCDD. Although the high resolution procedure has been valuable for gathering preliminary data on environmental TCDD levels, many factors militate against the use of this method on a routine basis.



We describe here a convenient low-resolution negative-ion chemical ionization mass spectrometric (CIMS) technique which is at least 25 times more sensitive than the high resolution procedure.[2a] Single ion monitoring on a 2 pg solid-probe sample of TCDD by the negative CIMS method affords a signal to noise ratio of $> 50:1$.

We have recently constructed a Townsend electric discharge (TED) ion source capable of operating over a pressure range of 1—760 Torr.[3] Unlike conventional ion sources which employ an electron beam generated by thermionic emission from a hot metal filament the TED source is unaffected by strong oxidizing reagents and affords negative and positive ion beams of comparable intensity.

With oxygen at 1 Torr as reagent gas and the TED source operating in the negative ion mode, O^- and O_2^- are produced in high abundance. Introduction of TCDD to this ion plasma affords a spectrum containing the molecular ion at *m/e* 320, and isotope clusters at *m/e* 176 ($M^- + O_2 - C_6H_2Cl_2O_2$), 301 ($M^- + O_2 - OCl$), and 335 ($M^- + O_2 - OH$). Formation of these ion–molecule reaction products presumably occurs by a sequence of events involving capture of a low energy electron by the TCDD molecule to give M^-, addition of an oxygen molecule to M^-, and subsequent elimination of either OCl, OH, or $C_6H_2Cl_2O_2$. Elimination of OCl[4] and OH[5] from adduct ions involving molecular oxygen and aromatic radical anions have been reported previously. The third reaction pathway is of particular interest here since it results from cleavage of the ether linkages in the TCDD molecule and affords an ion which is characteristic of structure, carries >80% of the sample ion current, and is well out of the mass range containing ions due to other contaminating chlorocarbons.[2] Since no overlap occurs with the TCDD spectrum, use of the negative-ion CIMS method with oxygen as the reagent gas should facilitate the analysis of TCDD under low resolution conditions in the presence of other chlorocarbon residues.

The above example illustrates one of the most powerful features of CIMS; namely, the ability to devise ion–molecule reactions to suit the needs of the analytical problem at hand. The nature and extent of fragmentation observed under CI conditions can be controlled by varying the type and energetics of the ion-molecule reaction employed in the ionization step.

This research was supported in part by National Science Foundation and the U.S. Army Research Office.

(*Received*, 11*th November* 1974; *Com.* 1371.)

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