Organic Peroxides

Using Reductive LCEC

Due to their excellent oxidizing, bleaching, and sterilizing properties, organic peroxides have found wide application in various industrial areas (1) such as pharmaceuticals, cosmetics, polymers, textiles, and dyes. Widely distributed throughout the food chain, peroxides and hydroperoxides are formed in food, vegetable oils, and soaps. They produce a distasteful odor in food oils and accelerate the decomposition process. In petrochemical distillation processes, peroxides, even at very low concentrations, can initiate polymeric reactions resulting in the formation of troublesome gums and sediments. Strong interest in peroxides is found in radiobiology and medicine where these compounds have been linked to cell damage caused by man-made or natural radiation.

A large number of analytical methods have been published for the determination of these compounds. Iodometric methods (2,3) have been very popular because of their simplicity; they are fairly non-specific. Several colorimetric methods (4,5) suffer from the same drawbacks. Gas chromatographic methods are usually unsuitable since the majority of inorganic peroxides demonstrate thermal instability; however, certain stable hydroperoxides, dialkyl peroxides, and peroxyesters have been determined by GC. Paper chromatography with spectroscopic (6) and colorimetric (7) detection has been utilized.

Most organic peroxides are electrochemically reducible at a mercury electrode and thus, in theory, amenable to detection by the LCEC technique. The reduction potential necessary depends on the structure of the compound. Relative to the standard Ag/AgCl or calomel reference electrodes, easily reduced compounds such as peroxy esters and acids may be detected at very low positive and negative potentials (typically +0.2 to -0.2 volts), presumably as a result of electronic delocalization.

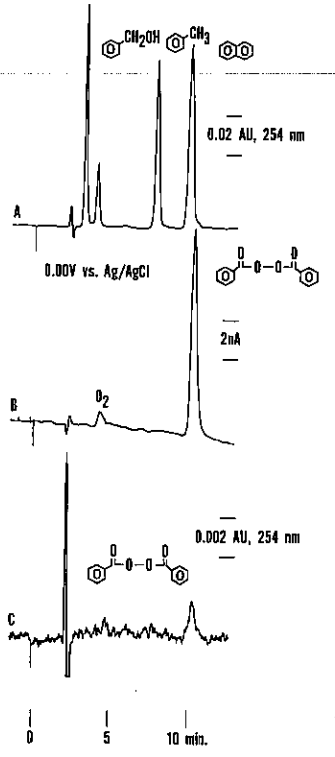

Figure 1. Chromatography of various aromatics, including the electroactive benzoyl peroxide, using a reverse phase system. (A) LCUV at 254 nm 0.20 AUFS. Mixture: benzyl alcohol, 16 µg; toluene, 13 µg; naphthalene, 1.5 µg; Benzoyl peroxide, 66 ng. (B) LCEC at 0.0 V vs. Ag/AgCl reference, 20 nA full scale. Mixture: same as (A). (C) LCUV at 254 nm, 0.02 AUFS. Sample: benzoyl peroxide, 66 ng. (Reprinted from reference 8 by permission of the copyright owner.)

Alkyl hydroperoxides and dialkyl peroxides require moderate or more rigorous reducing power(8).

Funk, Keller, and Levinson described the detection of several peroxides by LCEC using a TL-6A gold/mercury electrode. This cell configuration permits the application of a mercury film on a gold sub-

strate; the advantages of the thin-layer design are preserved. Lifetimes (usually 1-2 weeks) depend on the intactness of the mercury surface; once gold diffuses to the surface, the high hydrogen overpotential exhibited by mercury is lost. Resurfacing with additional mercury restores performance. Detection limits were on the order of 10 nanograms injected. Better performance can be expected using a BAS 200 chromatograph which incorporates a complete deoxygenation and temperature control system.

The selectivity and sensitivity of the electrochemical detector is clearly demonstrated in Figure 1. Trace A represents a multi-component, UV absorbing mixture containing 66 nanograms of benzoyl peroxide as well as toluene, benzyl alcohol and naphthalene. The acyl peroxide is the small shoulder on the tailing edge of naphthalene. Trace B shows the same mixture and separation, but with the electrochemical detector. A small oxygen peak - oxygen is reducible - along with a strong peroxide response is evident. The inherent selectivity of LCEC for only those substances reducible at this potential ensures a very clean chromatogram. Trace C demonstrates the marginal response of the 254 nm UV detector to 66 nanograms of benzoyl peroxide alone. A linearity plot from 10-250 nanograms injected yielded a correlation coefficient of 0.99998.

References

1. R. M. Johnson and I. W. Siddiqi, "The Determination of Organic Peroxides", in Monographs in Organic Functional Group Analysis, R. Belcher, D. M. W. Anderson, Eds., Permagon Press, London, 1970.

2. B. D. Scully and P. L. Williams, Analyst, 87(1962) 652.

3. K. Oette, M. L. Peterson and R. L. McAuley, J. Lipid Res., 4(1963) 212.

4. A. J. Martin, "Determination of Organic Peroxides in Organic Analysis," Interscience, N.Y., 1961, Vol IV.

5. A. Banderet, M. Brendle, and G. Reise, Bull. Soc. Chem. France, (1965) 625.

6. J. A. Brammer, S. Frost, and V. W. Reid, Analyst, 92(1967) 91.

7. W. E. Parker, C. Riccuitti, C. L. Ogg, and D. J. Swern, J.A.C.S., 81(1959) 3244.

8. M. O. Funk, M. B. Keller, and B. Levinson, Anal. Chem., 52(1980) 773.