

## Periodic Acid, a Novel Oxidant of Polycyclic Aromatic Hydrocarbons

By ALEXANDER J. FATIADI

(Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234)

TREATMENT of pyrene (I) with paraperiodic acid in aqueous acetic acid produces<sup>1</sup> the coupling product 1,1'-bipyrenyl (II) in over 70% yield.

In order to determine whether periodic acid<sup>2</sup> would serve as a general reagent for effecting similar coupling reactions, other polycyclic aromatic hydrocarbons were treated with this reagent. It was found that many of these hydrocarbons are affected by periodic acid; however, instead of coupling, oxidation to quinones occurs.

A solution of naphthacene (III) (1.15 g., 0.005 mole) in *NN*-dimethylformamide (100 ml.) was stirred with an aqueous solution of paraperiodic acid (4.6 g., 0.02 mole; 5 ml.) at 120° for 5 min. and then (to slow down the vigorous reaction) at 70° for 30 min. The reaction mixture was treated with water (50 ml.), and cooled to yield naphthacene-quinone (1.0–1.1 g.; 80–85%), m.p. 278–281°. After purification this was proved to be identical with an authentic sample<sup>3</sup> by mixture m.p., infrared spectrum, and thin-layer chromatography on silica gel G. Oxidation of (III) in glacial acetic acid proceeds also, but only in 40–50% yield.

Similarly, by use of an approximately 1:4 molar ratio of substrate to periodic acid, the following hydrocarbons were oxidized; anthracene in *NN*-dimethylformamide, at 95° for 5 min. and at 70° for 30 min., to anthraquinone (91–95%); naphthalene in glacial acetic acid, at 110° for 5 min. and at 70° for 30 min., to 1,4-naphthoquinone (70–76%); and phenanthrene in dioxan, at 95° for 5 min. and at 30° for 30 min., to phenanthrenequinone (50%). In the same way, benz[*a*]anthracene (in *NN*-dimethylformamide) was oxidized to benz[*a*]anthracene-7,12-dione (78–82%); pentacene (in *NN*-dimethylformamide) to pentacene-6,13-quinone (81–87%), and acenaphthene (in acetic acid) to acenaphthenequinone (65–70%). By use of a *ca.* 1:2 molar ratio of hydrocarbon to periodic acid, anthrone (in acetic acid) was oxidized to the quinone (94%). Little or no reaction was observed with biphenyl, perylene, coronene, *p*-terphenyl, and triphenylene, chrysene and picene.

When sodium metaperiodate was used instead of periodic acid, none of these reactions was observed. E.s.r. monitoring of the reaction of periodic acid on anthracene, either in aqueous acetic acid or aqueous *NN*-dimethylformamide (in the range

0–100°), indicated that there is no radical participation in the oxidation.

In contrast, dimerization of (I) to (II) proceeds through the radical intermediate, and the e.s.r. spectrum of this radical is shown in the Figure.

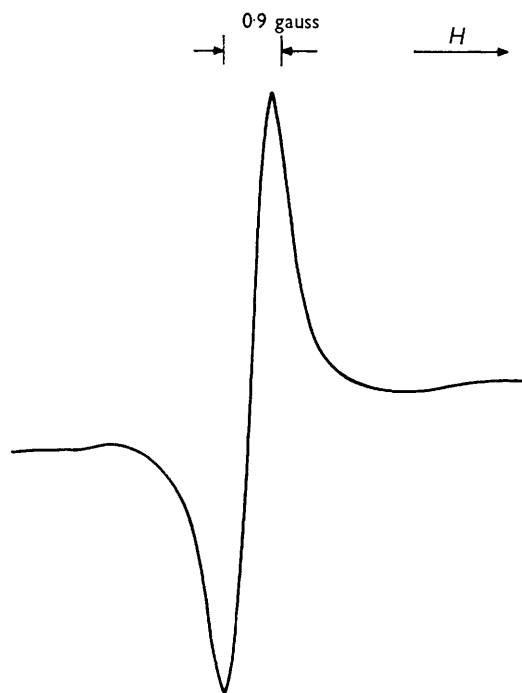


FIGURE. The e.s.r. spectrum of pyrene radical, prepared by treatment of pyrene (in acetic acid) with periodic acid,  $H_5IO_6$ , (in water) at room temperature,  $g = 2.0041$ .

As suggested previously,<sup>1</sup> the first step in the oxidations may involve association between periodic acid (an electrophile) and the free-valence centre<sup>4,5</sup> of the aromatic ring; this possibility is in agreement with the basicity of polycyclic aromatic hydrocarbons.<sup>6,7</sup>

Hence, the behaviour of periodic acid toward polycyclic aromatic hydrocarbons has a unique, two-fold character; it can produce coupling products through a radical intermediate, or quinones by a two-equivalent oxidation.

This work was supported by the Division of Air

Pollution, Public Health Service, U.S. Department of Health, Education, and Welfare. I thank Drs. R. Schaffer, H. S. Isbell, and R. S. Tipson for

their interest, and Drs. G. F. Kokoszka, M. Linzer, and N. Adams for the e.s.r. measurements.

(Received, July 26th, 1967; Com. 778.)

<sup>1</sup> A. J. Fatiadi, *J. Org. Chem.*, 1967, in the press.

<sup>2</sup> B. Sklarz, *Quart. Rev.*, 1967, **21**, 3.

<sup>3</sup> S. Gabriel and E. Leupold, *Ber.*, 1898, **31**, 1277; E. J. Moriconi, W. F. O'Connor, and L. B. Taranko, *Arch. Biochem. Biophys.*, 1959, **83**, 283.

<sup>4</sup> M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.

<sup>5</sup> B. Pullman and H. Pullman, *Progr. Org. Chem.*, 1958, **4**, 31.

<sup>6</sup> E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.

<sup>7</sup> A. Streitwieser, jun. and J. H. Hammons, *Progr. Phys. Org. Chem.*, 1965, **31**, 4.