

## Formation of Anthracene Cation Radicals from 9,10-Dihydro-9,10-epidioxyanthracene Derivatives; Peroxide-initiated Cationic Polymerization of Styrene in Liquid Sulphur Dioxide

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The formation of anthracene cation radicals from some 9,10-dihydro-9,10-epidioxyanthracene derivatives in liquid sulphur dioxide is reported. By use of catalytic amounts of 9,10-dihydro-9,10-epidioxyanthracenes, the cationic polymerization of styrene has been accomplished in liquid sulphur dioxide.

It has been reported that cationic polymerization of styrene takes place in the presence of anthracene in the liquid sulphur dioxide-oxygen system.<sup>1,2</sup> It was presumed that initial formation of a cation radical of anthracene took place, followed by formation of a styrene cation radical by electron transfer from styrene to the anthracene cation radical, and at that time it was suggested that the anthracene cation radical was produced by direct transfer of an electron from the hydrocarbon to an oxygen molecule.

We later found that perylene and pyrene, whose ionization potentials are comparable to that of anthracene,<sup>3</sup> did not initiate the polymerization of styrene. A notable difference between anthracene derivatives (I) and those of other aromatic hydrocarbons is the high reactivity of the former towards singlet oxygen.<sup>4</sup> We have therefore studied the behaviour of epidioxyanthracene peroxide derivatives (II) in liquid sulphur dioxide in order to discover whether they can yield the corresponding cation radicals, and also whether they can initiate the cationic polymerization of styrene in liquid sulphur dioxide.

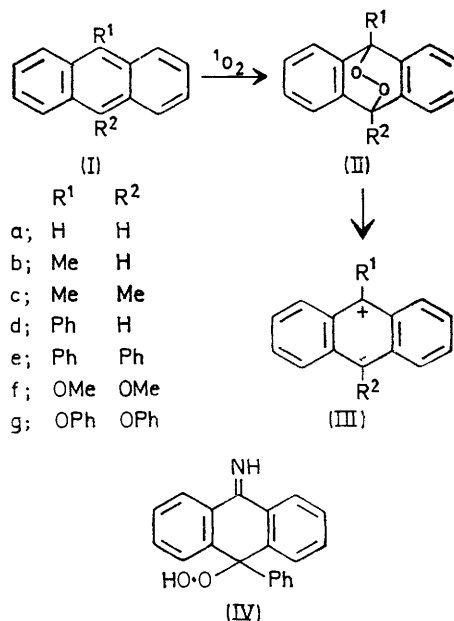
### RESULTS

When 9,10-dihydro-9,10-diphenyl-9,10-epidioxyanthracene (IIe) (10 mg,  $2.8 \times 10^{-2}$  mmol) was dissolved in liquid sulphur dioxide (5.5 ml) and the mixture was kept at room temperature in the dark and in the absence of oxygen, 9,10-diphenylanthracene cation radical (IIIe) was formed immediately, as indicated by the u.v.

<sup>1</sup> N. Tokura, T. Nagai, and Y. Sonoyama, *Tetrahedron Letters*, 1965, 1145.

<sup>2</sup> T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3087.

spectrum ( $\lambda_{\max}$ , 717, 650, 590, and 550 nm). The maximum yield, measured by the absorption at 717 nm,



was 20%. From the reaction mixture, 9,10-diphenylanthracene (Ie) was isolated in 40% yield after 48 h. The e.s.r. spectrum of (IIIe), showing 41 splittings, was identical with that obtained<sup>5</sup> from the product of the reaction of (Ie) with sulphuric acid in n-hexane.

<sup>3</sup> L. L. Miller, G. D. Norblom, and E. A. Mayeda, *J. Org. Chem.*, 1972, **37**, 916.

<sup>4</sup> R. W. Denny and A. Nickon, *Org. Reactions*, 1973, **20**, 133.

<sup>5</sup> L. O. Weeler, K. S. V. Santhanam, and A. J. Bird, *J. Phys. Chem.*, 1966, **70**, 404.

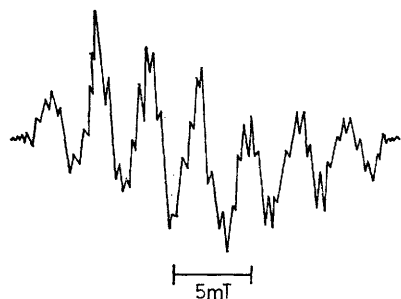
From the peroxides (IIc), (IIe), and (IV) the corresponding cation radicals were obtained under the same conditions and characterized by u.v. and e.s.r. spectroscopy (Table 1) [see Figure for the e.s.r. spectrum of the

TABLE 1

Formation of cation radicals from peroxides in liquid sulphur dioxide <sup>a</sup>

| Peroxide | $\lambda_{\max.}/\text{nm}$ | E.s.r. hyperfine splitting constant (mT)   | Recovery of hydrocarbons (%) |
|----------|-----------------------------|--|------------------------------|
| (IIc)    | 730                         | $a_{\text{H}}$ (6) 7.4 <sup>b,c</sup>  | 25                           |
| (IIe)    | 900                         | $d$  | 20                           |
| (IV)     | 717, 650, 590, 550          | $a_{\text{H}}$ (4) 2.76 <sup>e</sup><br>$a_{\text{H}}$ (4) 1.38<br>$a_{\text{H}}$ (2) 6.25 <sup>f</sup><br>$a_{\text{N}}$ (1) 3.15 | 40<br>14.5                   |

<sup>a</sup> Peroxide (5.6 mmol l<sup>-1</sup>) in liquid sulphur dioxide at 20 °C in the dark. <sup>b</sup> Approximate value for partially resolved spectrum. <sup>c</sup> A. Reymond and G. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 4570. <sup>d</sup> The spectrum consisted of 30 lines only partially resolved. Almost the same spectrum was obtained from the product of the reaction of (Id) with sulphuric acid. <sup>e</sup> L. O. Weeler and K. S. V. Santhanam, *J. Phys. Chem.*, 1966, **70**, 404. <sup>f</sup> J. Rigaudy, G. Cauguis, G. Izoret, and J. Baranne, *Bull. Soc. chim. France*, 1961, 1842.



E.s.r. spectrum of the cation radical (III; R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = Ph) from the peroxide (IV)

cation radical (III; R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = Ph)]. After work-up of the reaction mixtures, the corresponding hydrocarbons were recovered in yields of 25, 20, and 14.5%, respectively.

9,10-Dihydro-9,10-epidioxyanthracene (IIa) in liquid sulphur dioxide did not yield the anthracene cation radical, as observed by u.v. spectroscopy,\* and anthraquinone was obtained quantitatively as the final product. The presence of base resulted in different products. In the presence of an excess of pyridine anthracene (15%) was obtained, and the formation of 9-chloroanthracene (24%) was observed in the presence of tetraethylammonium chloride. Similarly, in the case of 9,10-dihydro-9-methyl-9,10-epidioxyanthracene (IIb), the formation of 9-methylanthracene cation radical was not detected by e.s.r. or u.v. spectroscopy but 9-methylanthracene was obtained in 25% yield after 48 h. The dimethoxy-peroxide (IIe) also did not yield a cation radical (IIIe), only anthraquinone being obtained (quantitatively). In contrast to the reaction of (IIa) anthraquinone was also obtained by the reaction of (IIe) in the presence of pyridine.

In the light of these results, the direct formation of cation radicals from (I) in the oxygen-sulphur dioxide

\* The e.s.r. spectrum consisted of three broad lines with splitting constant of 2.7 mT.

system by irradiation was examined. When a solution of 9,10-diphenoxyanthracene (Ig) (10.1 mg, 3.0 × 10<sup>-2</sup> mmol) and oxygen (5 ml) in sulphur dioxide (5 ml) in a quartz vessel was irradiated with a 300 W incandescent lamp at a distance of 20 cm at 0 °C, 9,10-diphenoxyanthracene cation radical (IIIg) was formed immediately, as indicated by the u.v. spectrum ( $\lambda_{\max.}$  670, 590, and 540 nm), and the intensity of the absorption increased as irradiation was continued. The e.s.r. spectrum, having 9 splittings and  $a_{\text{H}}$  1.0 mT, also suggested the formation of (III). 9-Amino-10-phenylanthracene (I; R<sup>1</sup> = NH<sub>2</sub>, R<sup>2</sup> = Ph) under the same reaction conditions also gave the cation radical (III). In the case of 9,10-diphenylanthracene the formation of (IIIe) was very slow and was first detected after 12 h. The need for both oxygen and light in cation radical formation from (I) was demonstrated. Under the same conditions, 9,10-dimethoxyanthracene did not yield the cation radical (IIIe), and anthraquinone was obtained in quantitative yield.

Peroxide-catalysed polymerizations of styrene were performed with compounds (IIa–f) to discover whether cationic polymerization occurs to give polystyrene or radical polymerization to give polysulphone. It is well known that most peroxides, like  $\alpha\alpha'$ -azobis(isobutyronitrile), can initiate the copolymerization of styrene and sulphur dioxide.<sup>6</sup> The results are collected in Table 2.

TABLE 2

Peroxide-initiated cationic polymerization of styrene in liquid sulphur dioxide <sup>a</sup>

| Initiator | Reaction time (h) | Yield of polystyrene (%) |
|-----------|-------------------|--------------------------|
| (IIa)     | 1.5               | 96                       |
| (IIb)     | 1.5               | 95                       |
| (IIc)     | 1.5               | 100                      |
| (IId)     | 4.0               | 9                        |
| (IIe)     | 4.0               | 0                        |
| (IIe)     | 4.0               | 78                       |

<sup>a</sup> Styrene (1 × 10<sup>-2</sup> mol) with peroxide (3 × 10<sup>-5</sup> mol) in sulphur dioxide (30 ml) at 0 °C.

Compounds (IIa–c, and f) initiate selectively the cationic polymerization of styrene, and these results are, to our knowledge, the first example of dialkyl peroxides initiating the cationic polymerization of styrene in liquid sulphur dioxide.† Polymerization of styrene was not effected by compounds (IIe and e).

These results suggest that 9,10-dihydro-9,10-epidioxyanthracene is the actual initiator of cationic polymerization of styrene in the oxygen-anthracene-sulphur dioxide system. With this in mind we reinvestigated the irradiation-induced polymerization of styrene in the oxygen-anthracene system. The results (Table 3) suggest that light is a necessity for this novel polymerization. Retardation of polymerization was observed when 9,10-diphenylanthracene was used as initiator, and this result agrees with the fact that the peroxide (IIe) has not the ability to initiate polymerization.

† From the u.v. spectra of the polymers, the existence of anthracene derivatives was detected when compounds (IIa–c) were used as initiators. In the case of (IIe) such absorption was not found.

<sup>6</sup> W. G. Barb, *J. Polymer Sci.*, 1953, **10**, 49.

TABLE 3

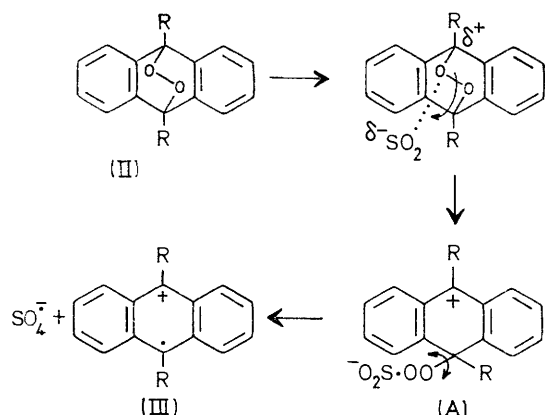
Irradiation-induced cationic polymerization of styrene in the anthracene derivative-oxygen-sulphur dioxide system<sup>a</sup>

| Initiator          | Reaction time (h) | Yield of polystyrene (%) |
|--------------------|-------------------|--------------------------|
| (IIa)              | 1.0               | 88                       |
| (IIa) <sup>b</sup> | 1.0               | 0                        |
| (IIe)              | 4.5               | 50                       |
| (IIe) <sup>b</sup> | 4.5               | 0                        |
| <sup>c</sup>       | 1.0               | 0                        |
| <sup>c</sup>       | 4.5               | 85                       |
| <sup>b, c</sup>    | 4.5               | 4                        |

<sup>a</sup> Styrene (10 mol) with compound (I) ( $2.0 \times 10^{-1}$  mmol) and oxygen (5 ml) in sulphur dioxide (5 ml); irradiation by 300 W incandescent lamp at distance of 20 cm at 0 °C. <sup>b</sup> The reaction was performed in the dark. <sup>c</sup> Initiator was not used.

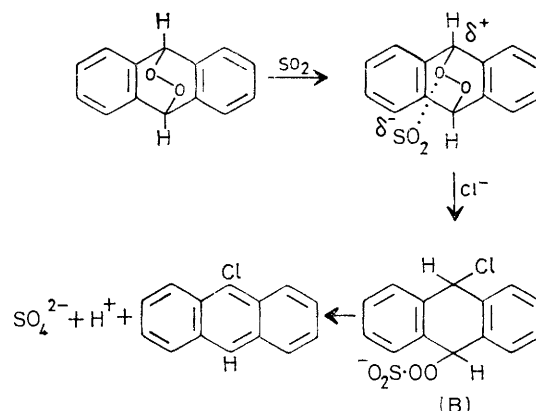
## DISCUSSION

For the formation of a cation radical from the peroxide, the following mechanism is considered the most probable. First sulphur dioxide, known to be a weak Lewis acid,<sup>7</sup> attacks an oxygen atom with heterolytic C-O fission to form intermediate (A). Compound (IIa) is well known to react with hydrogen chloride to give 10-chloro-9-anthrone through heterolytic C-O cleavage.<sup>8</sup> The intermediate (A) is not stable under our conditions, and the cation radical (III) is probably produced by homolytic fission of the other C-O bond. To investigate the possibility of heterolytic C-O fission by sulphur dioxide, we studied the reactions of bis(triphenylmethyl) peroxide and triphenylmethyl hydroperoxide with sulphur dioxide at room temperature for 12 h. U.v. spectroscopy showed the formation of triphenylmethyl cation ( $\lambda_{\max}$  410 and 430 nm) in yields of 12 and 69%, respectively.

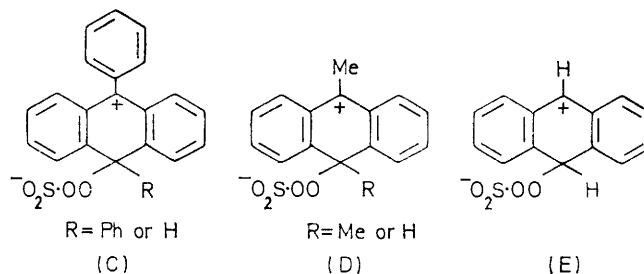


The fact that the peroxide (IIa) gave anthraquinone in the absence of nucleophile, but in the presence of pyridine anthracene was obtained in yield of 15%, suggests that pyridine can accelerate heterolytic C-O cleavage. A more clear-cut example of participation of a nucleophile in C-O fission is the formation of 9-chloroanthracene by the reaction of (IIa) with tetraethylammonium chloride. In liquid sulphur dioxide the intermediate (B) is not stable, and elimination of sulphate ion followed by deprotonation seems to occur to give the stable aromatic compound. For the cationic polymeriz-

ation of styrene the above process can reasonably be applied. Styrene, considered as the nucleophile, is able



to attack the intermediate (A) and then begins to polymerize. This mechanism satisfactorily explains why (II d and e) could not initiate the polymerization. The intermediates (C) from (II d and e) have the structure of triphenylmethyl cation, and triphenylmethyl cation itself, derived from bis(triphenylmethyl) peroxide, was found not to initiate the polymerization. From the peroxides (IIa-c) the formation of the intermediates (D) and (E), with structures similar to diphenylethyl cation and diphenylmethyl cation, is expected, and these



unstable intermediates can be attacked by styrene. Cation radicals are not excluded as the initiator of polymerization in our system, but for the following reasons we prefer a mechanism in which nucleophilic attack of styrene on the intermediates (D) and (E) is the initiation step. First, (IIa) did not give (IIIa) in liquid sulphur dioxide and so it is difficult to believe that (IIIa) is formed in the presence of a nucleophile like styrene. Secondly, dimethylantracene cation radical (III d),<sup>9</sup> but (II d) could not initiate the polymerization. From this result it is difficult to believe that (III d) cannot initiate the polymerization of styrene because of its own stability.

In the irradiation-induced reaction of anthracene derivatives with oxygen, it is reasonable to consider that singlet oxygen is formed first, followed by the anthracene peroxide derivative. Direct evidence for the formation of singlet oxygen in this system is difficult to obtain, but the necessity of light for the formation of

<sup>7</sup> A. J. Shipmann, B.P., 898, 630/1962.

<sup>8</sup> C. Dufraisse and M. Gerad, *Compt. rend.*, 1936, **202**, 1859.

<sup>9</sup> L. S. Marcoux, J. M. Fritsch, and R. N. Adams, *J. Amer. Chem. Soc.*, 1967, **89**, 5766.

radical cations from anthracene derivatives and also the polymerization of styrene suggest that this occurs. Furthermore the production of anthraquinone from 9,10-dimethoxyanthracene cannot be explained by the alternative mechanism. In this reaction the retarding effect of triethylamine, well known as a quencher of singlet oxygen,<sup>10</sup> was observed.

#### EXPERIMENTAL

<sup>1</sup>H N.m.r. spectra were obtained with a Nippon Denshi (JEOC) spectrometer (JNM 3H-60). U.v. spectra were run with a Varian Techron 635 spectrometer. E.s.r. spectra were obtained with a Nippon Denshi spectrometer (ME 2X). Details of the apparatus used for reactions in liquid sulphur dioxide have been described.<sup>2</sup>

*Materials.*— 9,10-Dihydro-9,10-epidioxyanthracene,<sup>11</sup> 9,10-dihydro-9-methyl-9,10-epidioxyanthracene,<sup>12</sup> 9,10-dihydro-9,10-dimethyl-9,10-epidioxyanthracene,<sup>5</sup> 9,10-dihydro-9-phenyl-9,10-epidioxyanthracene,<sup>13</sup> 9,10-dihydro-9,10-diphenyl-9,10-epidioxyanthracene,<sup>14</sup> 9,10-dihydro-9,10-dimethoxy-9,10-epidioxyanthracene,<sup>15</sup> and 9,10-dihydro-10-hydroperoxy-9-imino-10-phenylanthracene,<sup>15</sup> 9,10-diphenoxyanthracene,<sup>16</sup> 9-amino-10-phenylanthracene,<sup>15</sup> bis(triphenylmethyl) peroxide,<sup>17</sup> and triphenylmethyl hydroperoxide<sup>18</sup> were prepared by literature methods.

*Reaction of Peroxides in Liquid Sulphur Dioxide.*—Into a quartz cell containing the peroxide ( $2.8 \times 10^{-2}$  mmol) was distilled in the dark at  $-70^\circ\text{C}$ , sulphur dioxide (5.5 ml) which had been dried, distilled, and evacuated at  $10^{-5}$  mmHg. The solution was frozen (liquid nitrogen) and evacuated three times at  $10^{-5}$  mmHg, and the vessel was then warmed to  $20^\circ\text{C}$ . The formation of cation radicals was followed by u.v. spectroscopy. Samples for measurement of e.s.r. spectra were prepared by the same procedure.

After 48 h the mixture was cooled, diluted with water,

<sup>10</sup> W. F. Smith, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 186.

<sup>11</sup> C. S. Foote, S. Werler, W. Ando, and R. Higgins, *J. Amer. Chem. Soc.*, 1968, **90**, 975.

<sup>12</sup> A. Willemart, *Bull. Soc. chim. France*, 1938, 556.

<sup>13</sup> C. Dufraisse, L. Velluz, and L. Velluz, *Bull. Soc. chim. France*, 1937, 1260.

<sup>14</sup> H. H. Wasserman, J. R. Scheffr, and J. L. Cooper, *J. Amer. Chem. Soc.*, 1973, **94**, 4991.

and extracted three times with ether. The organic layer was washed with aqueous sodium hydroxide and saturated brine, and then dried ( $\text{Na}_2\text{SO}_4$ ). Products were isolated by column chromatography, and characterized by comparison of physical data with those of authentic samples.

The reaction of 9,10-dihydro-9,10-epidioxyanthracene ( $63 \text{ mg}$ ,  $3.0 \times 10^{-2}$  mol) was performed with pyridine ( $5.0 \times 10^{-2}$  mol) in sulphur dioxide (20 ml) at  $20^\circ\text{C}$  for 24 h, and from the reaction mixture anthracene (9.0 mg, 15%) was isolated by column chromatography. From the reaction of (IIa) ( $63 \text{ mg}$ ,  $3.0 \times 10^{-3}$  mol) and tetraethylammonium chloride ( $2.5 \text{ g}$ ,  $1.5 \times 10^{-2}$  mol) under the same conditions, 9-chloroanthracene (17.6 mg, 24%) was obtained.

The polymerization of styrene (10 mmol) was performed with the peroxide ( $3 \times 10^{-2}$  mmol) in sulphur dioxide (5 ml) at  $0^\circ\text{C}$ . The polymer was precipitated by addition to a large amount of methanol, and purified by reprecipitation from solution in benzene with methanol. Elemental analysis and i.r. spectra showed the lack of contamination by polysulphone.

*Irradiation-induced Reaction of Anthracene Derivatives in the Oxygen-Sulphur Dioxide System.*—A solution of the anthracene derivative ( $2.0 \times 10^{-2}$  mmol) and oxygen (5 ml) in sulphur dioxide (5 ml) in a quartz vessel was irradiated with a 300 W incandescent lamp at a distance of 20 cm at  $0^\circ\text{C}$ , and the formation of a cation radical was followed by u.v. spectroscopy. The reaction of 9,10-dimethoxyanthracene under these conditions for 20 h gave anthraquinone quantitatively, but in the presence of 4 equiv. of triethylamine only a 40% yield of anthraquinone was obtained.

The polymerization of styrene (10 mmol) in the presence of the anthracene (I) ( $2.0 \times 10^{-1}$  mmol) and oxygen (5 ml) in sulphur dioxide (30 ml) was performed under the same conditions.

[5/695 Received, 14th April, 1975]

<sup>15</sup> J. Rigaudy, G. Cauguis, G. Izoret, and J. Baranne, *Bull. Soc. chim. France*, 1961, 1842.

<sup>16</sup> A. Zweig, A. H. Maurer, and G. B. Roberts, *J. Org. Chem.*, 1967, **32**, 1322.

<sup>17</sup> H. R. Stelzner, *Ber.*, 1900, **33**, 3150.

<sup>18</sup> D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1964, **86**, 3824.