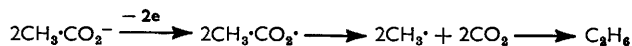


### 54. The Electrolysis of Some *o*-Benzoylbenzoic Acids in Methanol at 20—30°.

By P. J. BUNYAN and D. H. HEY.

The electrolysis of a series of five *o*-benzoylbenzoic acids in methanol at 20—30° has been investigated. Under these conditions internuclear cyclisation was observed only with the *o*-benzoylbenzoic acid, which gave fluoren-9-ol in very small yield, and with *o*-*p*'-bromobenzoylbenzoic acid, which gave 3-bromofluorenone. In all the electrolyses the main identified products were 3-arylphthalides and aryl methyl phthalates, the latter being formed by a rearrangement of the intermediate *o*-benzoylbenzoyloxy-radical.

THREE main theories have been put forward to explain the Kolbe reaction, with particular reference to the formation of ethane at the anode in the electrolysis of acetates. The peroxide theory, proposed by Schall<sup>1</sup> and developed by Fichter,<sup>2,3</sup> and the hydrogen peroxide theory of Glasstone and Hickling<sup>4</sup> have now been rejected in favour of the radical theory, which was first put forward in an elementary form by Crum Brown and Walker.<sup>5</sup> This theory envisages the discharge of the acetate anion at the anode, giving an acetoxy-radical, which then breaks down to give a methyl radical and carbon dioxide:



It has received support from the work of Clusius and his co-workers<sup>6,7</sup> on the electrolysis of carboxylic acids and deuterio-carboxylic acids in water and in deuterium oxide. These workers showed that the electrolysis of acetate solutions led to ethane, or at low current densities methane, the composition of either product depending only on the isotopic structure of the acetate ion and not on that of the solvent. This result is consistent with the formation of methyl radicals at the anode, which either dimerise, if they are present in high concentration at the anode surface, or abstract hydrogen from a molecule of acetic acid or an acetate ion. Methanol, if present, may act as a hydrogen donor. In all cases only carbon-hydrogen or carbon-deuterium bonds are broken, and it is postulated that the dehydrogenated fragments subsequently become oxidised at the anode to carbon dioxide and water. Similar studies<sup>8-10</sup> have shown that the olefins formed in the electrolysis of propionic and butyric acid arise from the intermediate free radicals by elimination of a hydrogen atom from the  $\beta$ -position in the original carboxylic acid. Stronger support for the radical theory has been provided by Lippincott and Wilson,<sup>11</sup> who used square-wave current for the electrolysis of acetate and propionate solutions in water and acetic acid at such a frequency that a steady state is never reached at the anode. These workers derived a relationship between the frequency of the current and the yield of product, which depends on the molecularity of the slow stage of the reaction at the anode. This showed that the electrolysis of acetates is unimolecular in both acetic acid and water and thus proceeds by the same mechanism in *both* solvents. The rate-determining stage is established as the unimolecular breakdown of acetoxy-radicals to methyl radicals and carbon dioxide. The latter conclusion is supported by the observation that the addition

<sup>1</sup> Schall, *Z. Elektrochem.*, 1896, **3**, 83.

<sup>2</sup> Fichter, *Trans. Electrochem. Soc.*, 1939, **75**, 309.

<sup>3</sup> Fichter, *Bull. Soc. chim. France*, 1934, **1**, 1585.

<sup>4</sup> Glasstone and Hickling, *J.*, 1934, 1878.

<sup>5</sup> Crum Brown and Walker, *Trans. Roy. Soc. Edinburgh*, 1891, **36**, 291.

<sup>6</sup> Hölemann and Clusius, *Z. phys. Chem. (Leipzig)*, 1937, **35**, B, 261.

<sup>7</sup> Clusius and Schanzer, *Z. phys. Chem. (Leipzig)*, 1943, **192**, A, 273.

<sup>8</sup> Hölemann and Clusius, *Ber.*, 1937, **70**, 819.

<sup>9</sup> Clusius and Schanzer, *Z. phys. Chem. (Leipzig)*, 1941, **190**, A, 241.

<sup>10</sup> Kruis and Schanzer, *Z. phys. Chem. (Leipzig)*, 1942, **191**, A, 301.

<sup>11</sup> Lippincott and Wilson, *J. Amer. Chem. Soc.*, 1956, **78**, 4290.

of anisole to the electrolysis of acetates results in the formation of *o*-acetoxyanisole, which suggests that the acetoxy-radical has a finite life.<sup>12</sup> Anodic acetoxylation and methylations in the aromatic series have been previously reported and in a number of cases analogous reactions take place with lead tetra-acetate, which in these reactions is known to undergo a homolytic breakdown into acetoxy and methyl radicals.<sup>13</sup> In addition, the electrolysis of fatty acid salts has been used as a source of alkyl radicals for addition reactions at carbon-carbon double bonds in dienes<sup>14,15</sup> and for the polymerisation of vinyl monomers.<sup>16,17</sup>

The inability of aromatic carboxylic acids (in which the carboxyl group is *directly* attached to the aromatic nucleus) to undergo the Kolbe reaction on electrolysis may be due to the relative stability of the benzoyloxy-radical at the temperatures normally used for this reaction, and/or to the high reactivity of the aryl radical, formed after loss of carbon dioxide, which preferentially attacks the solvent. If free aryl radicals are produced in these electrolyses it should be possible to detect their presence by the investigation of systems which lend themselves to intramolecular homolytic substitution. It is already well known that in many reactions of this type, relatively high yields can be obtained especially, for example, where the steric requirements for the reaction are favourable, as in Pschorr's classical phenanthrene synthesis. A study has therefore been made of the electrolysis of a series of *o*-benzoylbenzoic acids in order to find out if the *o*-benzoylbenzoyloxy-radical will give rise to an *o*-benzoylphenyl radical, which can then undergo intramolecular cyclisation with loss of a hydrogen atom to form a fluorenone. The formation of fluorenones by means of *o*-benzoylphenyl radicals (and the *o*-benzoylphenyl cation), prepared from the diazonium salts of 2-aminobenzophenones, has already been reported,<sup>18-22</sup> but attempts to prepare the peroxide of *o*-benzoylbenzoic acid as an alternative source of the *o*-benzoylphenyl radical have failed.<sup>23</sup> The present work should provide such an alternative source.

TABLE I.

Electrolyses of benzoylbenzoic acids (0.1M) in methanol at 20–30°.

Substituent at <i>p</i> -position	H	Cl	Br	Me	OMe
Acid not recovered (moles) .....	0.099	0.082	0.098	0.086	0.091
Fraction (i) (g.) .....	2.46	2.06	2.74	1.66	2.57
3-Arylphthalide (%) .....	12.7	12.8	1.0	20.0	10.5
Aryl methyl phthalate (%) .....	15.1	27.2	24.4	18.2	19.0
Substituted fluorenone (%) .....	0.0	0.0	9.4	0.0	0.0
Substituted fluoren-9-ol (%) .....	0.7	0.0	0.0	0.0	0.0

The experiments now reported were carried out in methanol containing sodium methoxide at temperatures between 20° and 30°. A preliminary experiment on the electrolysis of *o*-benzoylbenzoic acid in aqueous methanolic sodium hydroxide solution under the normal conditions for the Kolbe reaction gave only 3-phenylphthalide in 70% yield by normal reduction and loss of water. Subsequent electrolyses were carried out in dilute methanolic sodium methoxide. Formaldehyde was formed in all cases and a sticky nonconducting polymer was frequently deposited on the electrodes. The reactions were

<sup>12</sup> Hayashi and Wilson, Abstracts of papers presented at 126th meeting of the American Chemical Society, New York, 1954.

<sup>13</sup> Waters, "The Chemistry of Free Radicals," Oxford Univ. Press, 1948, p. 141.

<sup>14</sup> Smith and Gilde, *J. Amer. Chem. Soc.*, 1959, **81**, 5325.

<sup>15</sup> Lindsey and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2073.

<sup>16</sup> Goldschmidt and Stöckl, *Ber.*, 1952, **85**, 630.

<sup>17</sup> Smith and Gilde, *J. Amer. Chem. Soc.*, 1960, **82**, 659.

<sup>18</sup> DeTar and Sagmanli, *J. Amer. Chem. Soc.*, 1950, **72**, 965.

<sup>19</sup> Hey and Mulley, *J.*, 1952, 2276.

<sup>20</sup> DeTar and Relyea, *J. Amer. Chem. Soc.*, 1954, **76**, 1680.

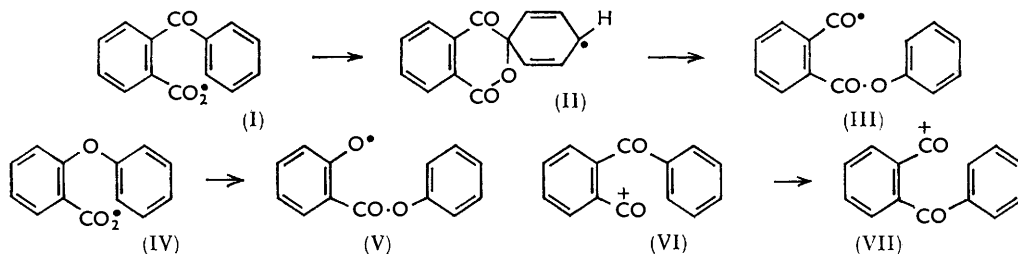
<sup>21</sup> DeTar and Whiteley, *J. Amer. Chem. Soc.*, 1957, **79**, 2498.

<sup>22</sup> DeTar, *Org. Reactions*, 1957, **9**, 409.

<sup>23</sup> DeTar and Chu, *J. Amer. Chem. Soc.*, 1960, **82**, 4969.

also complicated by the occurrence of reduction. Under these conditions the electrolyses did not in general lead to decarboxylation and intramolecular cyclisation, but instead revealed a novel type of molecular rearrangement.<sup>24</sup> The main results obtained with *o*-benzoylbenzoic acid and four *p*-substituted *o*-benzoylbenzoic acids are summarised in Table 1. Percentage yields are given for those products which were isolated quantitatively, the figures being based on the amount of acid not recovered at the end of the electrolysis. The current efficiency based on the assumption that all acid not recovered undergoes the initial reaction  $R\cdot CO_2^- \longrightarrow R\cdot CO_2\cdot + e$  is of the order of 15–18% and in all the electrolyses the total current passed was approximately 15 A/hr.

Only in the case of *o*-*p*'-bromobenzoylbenzoic acid was the fluorenone formed. With *o*-benzoylbenzoic acid itself a little fluoren-9-ol was isolated. The 3-arylphthalides obviously arise by reduction and lactone formation but the exact mechanism of the reduction remains uncertain. The low yield of 3-*p*-bromophenylphthalide coupled with the unexpected appearance of 3-bromofluorenone may be fortuitous. The most interesting result is the formation of the aryl methyl phthalates. The formation of these esters, which appears to be a general reaction, must involve a rearrangement of the *o*-benzoylbenzoyloxy-radical produced as the first step at the anode. At the comparatively low temperature under which it is formed in these electrolyses this radical is considered to be sufficiently stable to undergo the rearrangement (I)  $\longrightarrow$  (III) in which it is suggested that (II) is formed as an intermediate. Proof of the position of attack by the substituted benzoyloxy-radical in the stage (I)  $\longrightarrow$  (II) is established by the isolation in every case of methyl *p*-substituted-phenyl phthalates from *o*-(*p*-substituted benzoyl)benzoic acids. In agreement with the postulated free-radical mechanism the yields of the aryl methyl phthalates are greater in all cases with the substituted *o*-benzoylbenzoic acids.



DeTar and Hlynsky<sup>25</sup> have shown that phenyl salicylate is formed in the decomposition of *o*-phenoxybenzoyl peroxide. For this reaction these authors suggested a

TABLE 2.

Substituent at <i>p</i> -position	Constituents of fraction (i) (Table 1).		
	Ketone	Lactone	Ester
H	Benzophenone	Phthalide	Dimethyl phthalate
Cl	<i>p</i> -Chlorobenzophenone	"	Methyl phthalaldehyde
Br	<i>p</i> -Bromobenzophenone	"	Methyl <i>p</i> -bromobenzoate
Me	Phenyl <i>p</i> -tolyl ketone	"	Unidentified
OMe	nil	"	Methyl phthalaldehyde

similar type of rearrangement, which they represented as (IV)  $\longrightarrow$  (V). These rearrangements recall the well-known acid-catalysed Hyashi rearrangement, which in its simplest form can be represented as (VI)  $\longrightarrow$  (VII).<sup>26</sup>

Closely related reactions have been previously reported by Breederveld and Kooyman,<sup>27</sup>

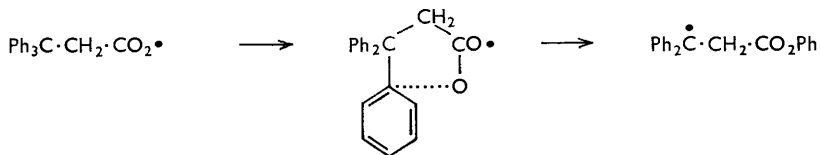
<sup>24</sup> Bunyan and Hey, *Proc. Chem. Soc.*, 1959, 366.

<sup>25</sup> DeTar and Hlynsky, *J. Amer. Chem. Soc.*, 1955, 77, 4411.

<sup>26</sup> Sandin, Melby, Crawford, and McGreer, *J. Amer. Chem. Soc.*, 1956, 78, 3817.

<sup>27</sup> Breederveld and Kooyman, *Rec. Trav. chim.*, 1957, 76, 297.

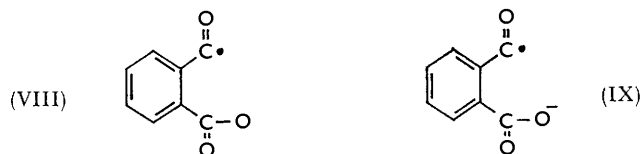
who investigated the electrolysis of  $\beta\beta\beta$ -triphenylpropionic acid and of  $\beta\beta\beta$ -tri-*p-t*-butylphenylpropionic acid in methanol. The former gave rise to the formation of the phenyl ester of  $\beta$ -methoxy- $\beta\beta$ -diphenylpropionic acid, which reaction was interpreted as involving a rearrangement of the acyloxy-radical in which an oxygen atom attacks an aromatic ring at its point of attachment to another carbon atom as follows:



In similar manner the  $\beta\beta\beta$ -tri-*p-t*-butylphenylpropionic acid gave the *p-t*-butylphenyl ester of  $\beta$ -methoxy- $\beta\beta$ -di-*p-t*-butylphenylpropionic acid, thus confirming the position of attack in the aromatic ring which undergoes rearrangement.

The components of fraction (i) in Table 1 vary in both magnitude and composition with the different acids (see Experimental Section). The three main constituents are in general a ketone, phthalide, and an ester, as summarised in Table 2. No quantitative estimation was possible.

The formation of the ketones presumably results from decarboxylation of the *o*-benzoylbenzoyloxy-radical followed by hydrogen abstraction from the solvent methanol. Under the experimental conditions here employed internuclear cyclisation with formation of the fluorenone is not favoured except, as reported above, in the reaction with *o-p'*-bromobenzoylbenzoic acid. The formation of phthalide and the esters probably results from a common intermediate such as (VIII) or (IX), but further speculation at this stage is not justified.



Electrolyses under similar conditions were carried out with *o*-phenoxybenzoic acid and *NN*-diphenylanthranilic acid, but no products resulting from internuclear cyclisation were observed.

#### EXPERIMENTAL

*Reagents.*—*o*-Benzoylbenzoic acid was prepared by Rubidge and Qua's method<sup>28</sup> and the air-dried hydrated acid was boiled under reflux with benzene. The water layer was removed, and the dried ( $\text{MgSO}_4$ ) benzene solution was concentrated. The hot solution was diluted with light petroleum (b. p. 80–100°) until a turbidity appeared. Anhydrous *o*-benzoylbenzoic acid separated, m. p. 129°. *o-p'*-Chlorobenzoylbenzoic acid, m. p. 152–153°, was prepared by Groggins and Newton's method,<sup>29</sup> *o-p'*-bromobenzoylbenzoic acid, m. p. 173°, by Ullmann and Sone's method,<sup>30</sup> and *o-p'*-tolylbenzoic acid, m. p. 138–139°, by McMullen's method.<sup>31</sup> *o-p'*-Hydroxybenzoylbenzoic acid, m. p. 217°, prepared from phenolphthalein by Orndoff and Murray's method,<sup>32</sup> was converted into *o-p'*-methoxybenzoylbenzoic acid, m. p. 147–148°, as described by Blicke and Weinkauff.<sup>33</sup> *o*-Phenoxybenzoic acid, m. p. 113–114°, was

<sup>28</sup> Rubidge and Qua, *J. Amer. Chem. Soc.*, 1914, **36**, 732.

<sup>29</sup> Groggins and Newton, *J. Ind. Eng. Chem.*, 1929, **21**, 369.

<sup>30</sup> Ullmann and Sone, *Annalen*, 1911, **380**, 337.

<sup>31</sup> McMullen, *J. Amer. Chem. Soc.*, 1921, **43**, 1965.

<sup>32</sup> Orndoff and Murray, *J. Amer. Chem. Soc.*, 1917, **39**, 679.

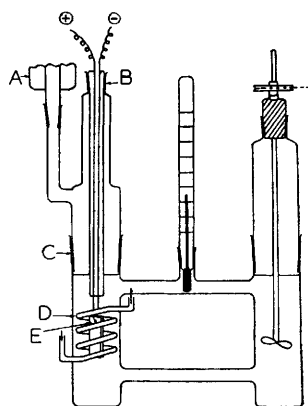
<sup>33</sup> Blicke and Weinkauff, *J. Amer. Chem. Soc.*, 1932, **54**, 330.

prepared by Brewster and Strain's method<sup>34</sup> and *NN*-diphenylanthranilic acid, m. p. 209—210°, by Goldberg and Nimerovsky's method.<sup>35</sup>

The aryl methyl phthalates were prepared by Dvornikoff's method.<sup>36</sup> Methyl phenyl phthalate had b. p. 134°/0.01 mm. (Found: C, 70.5; H, 4.8. Calc. for  $C_{15}H_{12}O_4$ : C, 70.3; H, 4.7%). *p*-Chlorophenyl methyl phthalate had b. p. 146°/0.02 mm. (Found: C, 61.95; H, 4.0.  $C_{15}H_{11}ClO_4$  requires C, 62.0; H, 3.8%). *p*-Bromophenyl methyl phthalate had m. p. 71°, b. p. 146°/0.01 mm. (Found: C, 53.7; H, 3.3.  $C_{15}H_{11}BrO_4$  requires C, 53.8; H, 3.3%). Methyl *p*-tolyl phthalate had m. p. 53°, b. p. 138°/0.01 mm. (Found: C, 71.1; H, 5.1.  $C_{16}H_{14}O_4$  requires C, 71.1; H, 5.2%). *p*-Methoxyphenyl methyl phthalate had m. p. 65.5°, b. p. 144°/0.01 mm. (Found: C, 67.2; H, 4.95; OMe, 22.0.  $C_{16}H_{14}O_5$  requires C, 67.1; H, 4.9; OMe, 21.8%).

3-Phenylphthalide, m. p. 118° (Found: C, 79.8; H, 4.7. Calc. for  $C_{14}H_{10}O_2$ : C, 80.0; H, 4.8%), was prepared by Ullmann's method<sup>37</sup> and fluoren-9-ol, m. p. 158° (Found: C, 85.8; H, 5.9. Calc. for  $C_{13}H_{10}O$ : C, 85.7; H, 5.5), by Kerp's method.<sup>38</sup> The earlier workers reported m. p. 115° and 156°, respectively.

*Apparatus.*—Current was provided by a transformer and rectifier which supplied 120 volts D.C. from the mains. Incorporated in the supply unit were a voltmeter, ammeter, and reversing switch, and the unit was connected in series with a rheostat. The cell employed, which is



A: Reflux condenser; B: B19 Standard joint;  
C: B40 Standard joint; D: Water cooling  
coil; E: Platinum electrodes.

illustrated diagrammatically in the Figure, consisted of two limbs, in one of which was a stirrer while the other contained a pair of smooth platinum sheet electrodes ( $4.2 \times 1.4$  cm.) kept 0.35 cm. apart and surrounded by a cooling coil. A thermometer in the upper cross-limb provided a measure of the internal temperature. A reflux condenser permitted electrolyses to be carried out at higher temperatures without loss of solvent. All electrolyses in methanol were carried out with the cell unit immersed, to just below the upper cross-limb, in a bath of ice and water.

*Electrolyses in Methanol at 20—30°.*—*o*-Benzoylbenzoic acid. The acid (22.6 g.; 0.1M) in methanol (280 ml.) containing sodium (0.23 g.) was electrolysed with the cell maintained in iced water. A current of 0.9—1.1 A was maintained for 12 hr. and thereafter one of about 0.75 A for 3 hr. To minimise the building up of a sludge the electrodes were constantly reversed and after 7 hr. they were mechanically cleaned. The voltage was gradually increased from 60 to 120 v. The internal temperature of the electrolyte remained at 24° throughout and the pH was 4.5. The solution gradually became dark and solid matter collected which appeared to be formed on the electrode acting as the anode. The contents of the cell, which had a pungent odour, were filtered. The residue, a pale brown amorphous solid A (1.32 g.), was dried at 70°. It was insoluble in all common solvents and did not melt below 340°. Removal of methanol from the filtrate left a brown oil. The methanol contained formaldehyde (dimerone derivative, m. p. and mixed m. p. 192°). The brown oil was extracted with boiling ether ( $5 \times 200$  ml.).

<sup>34</sup> Brewster and Strain, *J. Amer. Chem. Soc.*, 1934, **56**, 117.

<sup>35</sup> Goldberg and Nimerovsky, *Ber.*, 1907, **40**, 2448.

<sup>36</sup> Dvornikoff, U.S.P. 1,899,919.

<sup>37</sup> Ullmann, *Annalen*, 1896, **291**, 17.

<sup>38</sup> Kerp, *Ber.*, 1896, **29**, 228.

During this extraction a brown amorphous solid B (6.9 g.) was deposited. The combined ethereal extracts were washed successively with 2*N*-aqueous sodium hydroxide (10 × 20 ml.) and with water (3 × 50 ml.), and then dried (MgSO<sub>4</sub>) (neutral extract C). The brown amorphous solid B was dissolved in the alkaline washings; acidification of the ice-cooled solution with 20% hydrochloric acid gave a light brown solid, which was collected and dissolved in chloroform (200 ml.). The filtrate was also extracted with chloroform (10 × 20 ml.) and all the chloroform solutions were combined, and washed with water. After removal of chloroform the residue was kept overnight with a saturated aqueous solution of sodium bicarbonate (250 ml.), and the phenols were extracted with chloroform (5 × 20 ml.), and the extracts were washed and dried (MgSO<sub>4</sub>). Acidification of the bicarbonate solution liberated the acids, which were also extracted with chloroform (5 × 20 ml.), washed, and dried (MgSO<sub>4</sub>). Removal of the chloroform under reduced pressure from the phenolic extract gave a brown gum (2.0 g.). The acidic extract, under similar treatment, also gave a brown gum (6.5 g.), which was boiled with ethanol (charcoal). After filtration and removal of the ethanol under reduced pressure, the resulting solid crystallised from benzene–light petroleum (b. p. 80—100°) to give *o*-benzoylbenzoic acid (0.4 g.), m. p. and mixed m. p. 120—126°. The ethanol-insoluble material (6.1 g.) is probably an acidic polymer.

Removal of ether from the neutral extract C left a red viscous oil, which on distillation gave (i) a pale green liquid (2.46 g.), b. p. 84°/0.03 mm., which had an ethereal odour and slowly turned brown; (ii) a yellow oil (0.76 g.), b. p. 98°/0.03 mm., which partially solidified on ice; (iii) a viscous yellow-green oil (6.71 g.), b. p. 134°/0.03 mm.; and (iv) a red gum (0.53 g.), b. p. ca. 160°/0.05 mm. The residue weighed 0.84 g.

*Fraction (i)*: the infrared absorption spectrum showed the presence of ester and ketonic carbonyl groups. Hydrolysis of a portion of the oil with aqueous methanolic potassium hydroxide gave a product from which benzophenone (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 244—245°), phthalide, m. p. and mixed m. p. 73—74°, and phthalic acid, m. p. and mixed m. p. 196—199°, were isolated. A mixture of benzophenone, phthalide and dimethyl phthalate (1 : 1 : 2) showed an infrared absorption spectrum identical with that of fraction (i).

*Fraction (ii)*: recrystallisation from benzene–light petroleum (b. p. 80—100°) gave fluoren-9-ol, m. p. and mixed m. p. 157—158°.

*Fraction (iii)*: the slow addition of light petroleum (b. p. 60—80°) (40 ml.) to a warm solution of this fraction in benzene (10 ml.) deposited, on cooling to 0°, needles (2.61 g.) which on recrystallisation from benzene–light petroleum (b. p. 80—100°) gave 3-phenylphthalide in needles, m. p. and mixed m. p. 118°. The identity was confirmed by its infrared spectrum. The solvents were removed from the filtrate and the residue was collected at 134°/0.02 mm. as an orange-red oil (3.81 g.), which showed a strong ester band in the infrared spectrum. Hydrolysis of a portion of the oil with 10% aqueous sodium hydroxide gave phenol (benzoate, m. p. and mixed m. p. 65—67°) and phthalic acid, m. p. and mixed m. p. 193—194°. A second portion of the oil was treated with 3,5-dinitrobenzoic acid in the presence of a drop of concentrated sulphuric acid, as described by Renfrow and Chaney,<sup>39</sup> when methyl 3,5-dinitrobenzoate was obtained, m. p. and mixed m. p. 107.5—108.5°. The identity of the methyl phenyl phthalate was confirmed by its infrared spectrum, which was identical with that of an authentic specimen.

The following electrolyses were carried out on a tenth molar scale exactly as described above for *o*-benzoylbenzoic acid and the products were worked up in the same way. Details of the products obtained in all the electrolyses are summarised in Table 3.

*o*-*p*'-Chlorobenzoylbenzoic acid. A current of 1 A was maintained for 15 hr., the initial voltage being 44 v which was slowly raised to 82 v. The internal temperature was 22—28° and the pH 4.0. The solution became orange in colour and a little solid collected at the anode. Formaldehyde was formed during the electrolysis. The neutral fractions were collected as follows: (i) a pale yellow oil (2.06 g.) with an ethereal odour, b. p. 84—90°/0.03 mm.; (ii) a yellow-brown viscous oil (9.12 g.), b. p. 152°/0.03 mm.; (iii) a red gum (0.66 g.), b. p. ca. 170°/0.03 mm. The residue weighed 1.30 g. Hydrolysis of fraction (i) gave a product from which *p*-chlorobenzophenone, m. p. and mixed m. p. 74—75°, phthalide, m. p. and mixed m. p. 73—74°, and phthalaldehydic acid, m. p. and mixed m. p. 96—97°, were isolated. This fraction was regarded as a mixture of *p*-chlorobenzophenone, phthalide, and methyl phthalaldehyde, and

<sup>39</sup> Renfrow and Chaney, *J. Amer. Chem. Soc.*, 1946, **68**, 150.

was confirmed as such by means of infrared spectroscopy. Fraction (ii) gave 3-*p*-chlorophenylphthalide (2.58 g.) in needles from benzene–light petroleum (b. p. 80—100°), m. p. 124—125° (Found: C, 68.5; H, 3.7. Calc. for C<sub>10</sub>H<sub>9</sub>ClO<sub>2</sub>: C, 68.7; H, 3.7%) (O'Brochta and Lowy<sup>40</sup> have recorded m. p. 124° for this compound), and *p*-chlorophenyl methyl phthalate. The latter on hydrolysis gave *p*-chlorophenol, m. p. and mixed m. p. 38—40° (3,5-dinitrobenzoate, m. p. 188—189°; *p*-nitrobenzoate, m. p. 172—173°), and phthalic acid. The presence of a methyl ester was confirmed by Renfrow and Chaney's method.<sup>39</sup>

*o-p'*-Bromobenzoylbenzoic acid. A current of 1 A was maintained for 15 hr. and the initial voltage of 54 v was slowly raised to 102 v. The internal temperature was 26—30° and the pH remained constant at 5. The electrolyte became orange in colour and a white solid collected both on the anode and in solution. Formaldehyde was formed. Distillation of the neutral fraction gave: (i) a mobile liquid (2.74 g.), b. p. 86—94°/0.01 mm.; (ii) yellow needles (4.51 g.), b. p. 115°/0.01 mm.; (iii) a pale yellow viscous oil (8.41 g.), b. p. 146°/0.01 mm.; and (iv) a red gum (0.88 g.), b. p. ca. 180°/0.03 mm. The residue weighed 4.01 g. Hydrolysis of a portion of fraction (i) gave a product from which *p*-bromobenzophenone, m. p. and mixed m. p. 77—79°; phthalide, m. p. and mixed m. p. 73—74°; and slightly impure *p*-bromobenzoic acid were isolated. Recrystallisation of fraction (ii) from benzene–methylcyclohexane gave 3-bromo-fluorenone in fine yellow needles, m. p. and mixed m. p. 156—162°. Crystallisation of fraction (iii) from benzene–light petroleum (b. p. 80—100°) gave *p*-bromophenyl methyl phthalate, m. p. and mixed m. p. 69—71°, and slightly impure 3-*p*-bromophenylphthalide, m. p. 132—134° (Found: C, 57.5; H, 3.5. Calc. for C<sub>14</sub>H<sub>9</sub>BrO<sub>2</sub>: C, 57.95; H, 3.1%). Bergmann and Loewenthal<sup>41</sup> have reported m. p. 139—140° for this compound. The identity of these products was confirmed by infrared spectroscopy.

*o-p'*-Toluyloylbenzoic acid. A current of 0.8—1.2 A was maintained for 12 hr. and of 0.75 A for the final 3 hr. The voltage was varied from 54 v to 120 v. The internal temperature was 24—28° and the pH remained constant at 5. Distillation of the neutral fraction gave: (i) a pale green oil (1.66 g.), b. p. 96°/0.02 mm.; (ii) an orange-yellow viscous oil (8.64 g.), b. p. 140°/0.01 mm.; and (iii) an orange gum (0.62 g.), b. p. ca. 180°/0.03 mm. The residue weighed 1.32 g. Hydrolysis of a portion of fraction (i) gave a product from which phenyl *p*-tolyl ketone, m. p. and mixed m. p. 45—55° (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 203—204°), and phthalide, m. p. and mixed m. p. 73—74°, were isolated. Fraction (ii) on crystallisation from benzene–light petroleum (b. p. 60—80°) gave 3-*p*-tolylphthalide, m. p. 131° (Found: C, 80.7; H, 5.6. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>: C, 80.4; H, 5.4%). Dalev<sup>42</sup> has reported m. p. 130° for this compound. The mother liquors on redistillation and subsequent recrystallisation from benzene–light petroleum (b. p. 80—100°) gave methyl *p*-tolyl phthalate, m. p. and mixed m. p. 49—53°. The identity of these products was confirmed by infrared spectroscopy.

*o-p'*-Methoxybenzoylbenzoic acid. A current of 1 A was maintained during 15 hr., the voltage being increased from 52 v to 62 v. The internal temperature remained at 22° and the pH at 5. The electrolyte became golden-red and a small quantity of solid collected at the anode. Formaldehyde was formed. Distillation of the neutral fraction gave: (i) a pale green oil (2.57 g.) with an ethereal odour, b. p. 80°/0.01 mm.; (ii) a pale yellow oil (0.46 g.), b. p. ca. 90°/0.01 mm.; (iii) an orange-yellow viscous oil (7.41 g.), b. p. 152°/0.02 mm.; and (iv) a red gum (0.48 g.), b. p. 176°/0.02 mm. The residue weighed 1.51 g. From the product of the hydrolysis of fraction (i) *p*-methoxybenzophenone was not isolated but phthalide, m. p. and mixed m. p. 73—74°, and phthalaldehydic acid, m. p. and mixed m. p. 97—98°, were obtained. Crystallisation of fraction (iii) from benzene–light petroleum (b. p. 60—80°) gave 3-*p*-methoxyphenylphthalide, m. p. 117—118° (Found: C, 74.7; H, 5.2. Calc. for C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>: C, 74.9; H, 5.4%). Brubaker and Adams<sup>43</sup> have reported m. p. 117.5—118.5° for this compound. Distillation of the mother liquor at 172°/0.06 mm. gave an oil, which was chromatographed on neutral alumina (Woelm) in light petroleum (b. p. 60—80°). Elution with benzene–light petroleum (b. p. 60—80°) gave *p*-methoxyphenyl methyl phthalate, m. p. and mixed m. p. 64.5—65.5°. The identity of all products was confirmed by infrared spectroscopy.

Similar electrolyses were attempted with (a) *o*-phenoxybenzoic acid (21.42 g.) and (b) *NN*-di-phenylanthranilic acid (29.03 g.). In the former case *o*-phenoxybenzoic acid (8.78 g.) was

<sup>40</sup> O'Brochta and Lowy, *J. Amer. Chem. Soc.*, 1939, **61**, 2765.

<sup>41</sup> Bergmann and Loewenthal, *Bull. Soc. chim. France*, 1952, 66.

<sup>42</sup> Dalev, *Annuaire Univ. Sofia, Fac. phys.-math.*, Livre II, **41**, 37 (*Chem. Abs.*, 1955, **49**, 4594).

<sup>43</sup> Brubaker and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 2279.

TABLE 3.  
Products of electrolysis from 0.1M-acid.

Benzoic acid	Neutral products			Acid and polymeric products			
	1	2	3	4	5	6	7
<i>o</i> -Benzoyl- .....	2.46	2.61	3.81 *	1.32	2.0	0.4	6.1
<i>o-p'</i> -Chlorobenzoyl- .....	2.06	2.58	6.48	0.15	1.2	4.7	5.0
<i>o-p'</i> -Bromobenzoyl- .....	2.74	0.27	8.00 †	2.40	1.82	0.7	3.36
<i>o-p'</i> -Toluoyl- .....	1.66	4.06	4.46	0.61	1.40	3.2	4.7
<i>o-p'</i> -Methoxybenzoyl- .....	2.57	2.35	4.81	0.18	1.33	1.68	7.32

\* This reaction also gave fluoren-9-ol (0.126 g.). † This reaction also gave 3-bromofluorenone (2.38 g.).

Column headings: 1, fraction (i) (g.); 2, 3-arylphthalide (g.); 3, aryl methyl phthalate (g.); 4, solid A (g.); 5, phenols (g.); 6, recovered acid (g.); 7, acidic polymer (g.).

recovered and a further quantity of the same acid was obtained on hydrolysis of a neutral fraction (0.71 g.), b. p. 94°/0.02 mm. In addition, acidic polymer (8.1 g.) was formed. Phenyl salicylate was not detected (cf. ref. 25). In the latter case, in which some of the acid remained undissolved, the product consisted largely of unchanged acid (12.66 g.) and an acidic polymer (10.74 g.). No other products could be identified in these reactions.

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