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## **Degradation of Polycarbonates**

## II. Effect of Radiation on Model Compounds\*

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### SUMMARY:

The synthesis of a series of model compounds related to poly[2,2-propane-bis(4-phenyl)carbonate] is described. Exposure of these compounds to electron beam irradiation and analysis of the products has shown that degradation occurs predominantly at the carbonate grouping; reaction schemes are proposed for the products isolated. On the basis of these results and earlier work the radiation stability of the polymer is attributed mainly to its aromatic character, but it is suggested that radical recombination reactions are an important factor in reducing the degree of chain scission.

#### ZUSAMMENFASSUNG:

Die Synthese einer Reihe von Modellsubstanzen für Poly[2,2-Propan-bis(4-phenyl)carbonat] wird beschrieben. Läßt man auf diese Substanzen Elektronenstrahlen einwirken und analysiert die Produkte, so zeigt sich, daß der Abbau vornehmlich an der Carbonatgruppe geschieht; für die isolierten Produkte werden Reaktionsgleichungen angegeben. Auf Grund dieser Ergebnisse und früherer Arbeiten wird die Stabilität des Polymeren hauptsächlich seinem aromatischen Charakter zugeschrieben; man kann jedoch auch annehmen, daß Radikalrekombinationen einen wichtigen Faktor darstellen, um das Ausmaß der Kettenspaltung herabzusetzen.

## 1. Introduction

Little information has been published on the chemistry of the breakdown of polycarbonates by ionising radiation. Evidence so far obtained 1-5) has indicated that poly[2,2-propane-bis(4-phenyl)carbonate] undergoes chain scission and that no cross-linking occurs, the gaseous products formed being derived primarily from the carbonate linkage. Similarly, the radiation-induced decomposition of simple organic carbonates has not been studied in detail although some recent work has described the thermal<sup>6,7</sup>) and photolytic<sup>8</sup> decomposition of aliphatic carbonates.

<sup>\*)</sup> For Part I see ref. 5.

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It was decided therefore to obtain further information on the degradation of polycarbonates by the synthesis and subsequent degradation of various model compounds containing the functional groups present in poly[2,2-propane-bis(4-phenyl)carbonate], e.g.,

in addition, the effects of the functional groups would be considered separately in the decomposition of 2,2-diphenyl propane and diphenyl carbonate.

## 2. Experimental

### 2.1 Preparation of Model Compounds

## (a) 2,2-Diphenylpropane

Acetone (180 g.) in ether (500 ml.) was added to a vigorously stirred, cooled solution of phenyl lithium (252 g.) in ether (3.1) during 2 hrs. The solution was washed with water, dried and concentrated to yield crude 2-phenyl propan-2-ol (339 g., 83%). Distillation gave the pure alcohol (> 95%) b.p.<sub>0.25</sub> 53°C.,  $n_D^{18}$  1.5246, m.p. 24°C. (raised to 31-32°C. after standing on porous tile, as described by PERKIN<sup>9</sup>),

Condensation of the alcohol (265 g.) (or of 2-chloro-2-phenyl propane prepared by the method of BADDELEY<sup>10</sup>) with benzene in the presence of aluminium chloride<sup>11, 12</sup>) gave a brown hydrocarbon oil (249 g.) which was fractionated through a column packed with DIXON gauze rings to give 2,2-diphenylpropane b.p.<sub>0.01</sub> 97-98°C., m.p. 27°C.,  $n_D^{21}$  1.5691 (final purification effected by preparative vapour phase chromatography) and 1,1,3-trimethyl-3-phenyl hydrindene m.p. 52°C.,  $n_D^{20}$  1.5655. Minor quantities of an unsaturated hydrocarbon b.p.<sub>744</sub> 200-201°C.,  $n_D^{23}$  1.5352 (found: C 90.7 H 9.4) and, in the residue, of 3,3,3',3'-tetramethyl-1,1'-spiro-bi-indane m.p. 132°C. (CURTIS and LEWIS<sup>13)</sup> quote m.p. 133-134°C.)

(C<sub>21</sub>H<sub>24</sub> (276.4) Calcd. C 91.2 H 8.8 Found C 91.0 H 9.0)

were also isolated.

### (b) 1,1-Diphenyl-ethylene

Reaction of acetophenone (252 g.) with phenyl lithium (168 g.) as under (a) and recrystallisation of the crude product from cyclohexane gave 1,1-diphenyl-ethanol (317 g., 80%) m.p. 80°C. (KLAGES<sup>14)</sup> quotes m.p. 81°C.).

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Dry hydrogen chloride was bubbled through a solution of the alcohol (100 g.) in petrol (500 ml., b.p. 40-60 °C.) containing calcium chloride (50 g.) at -2 °C. during 1 hr. The solution was washed with water, dried and concentrated. The resultant oil was dissolved in tetrahydrofuran (250 ml.) and added dropwise to a stirred solution of methyl magnesium iodide (84 g.) in tetrahydrofuran (1 l.) during 1 hr. The solution was refluxed for 5 hrs., decomposed with ice, washed, dried, concentrated and distilled to give 1,1-diphenyl-ethylene (79 g., 87%) m.p.  $6.5^{\circ}$ C.,  $n_{17}^{17}$  1.6091.

# (c) 2(4-Hydroxyphenyl)2-phenyl propane

Prepared by condensation of 2-phenylpropan-2-ol with phenol<sup>15, 16)</sup> as colourless prisms, m.p. 72-73 °C. (yield 75%).

## (d) Sodium aryloxides

Prepared from the corresponding phenols as described by GOLDEN<sup>17</sup>).

## (e) 4,4'-Bis(phenoxycarbonyl)-dioxy biphenyl

Disodium salt of 4,4'-dihydroxybiphenyl. (4.6 g.) and phenyl chloroformate (6.3 g.) in ether (500 ml.) were refluxed for 12 hrs. and added to water (500 ml.). Filtration yielded the ester (4.6 g., m.p.  $170 \,^{\circ}$ C.) which gave microscopic needles (from benzene) m.p.  $172 \,^{\circ}$ C.

(C<sub>26</sub>H<sub>18</sub>O<sub>6</sub> (426.4) Calcd. C 73.2 H 4.3 Found C 73.3 H 4.3)

The ether liquors yielded further ester (0.5 g., total yield 60%).

## (f) 2,2-Bis(4-chloroformyloxyphenyl)-propane

Addition of a slurry of 2,2-bis(4-hydroxyphenyl)propane disodium salt (86 g.) in toluene (1 l.) during 2 hrs. to a stirred solution of excess phosgene in toluene (1 l.) at  $-15^{\circ}$ C., filtration, removal of solvent, and crystallisation of the residual oil (123 g.) from petrol (b.p.  $40-60^{\circ}$ C.) yielded 2,2-bis(4-chloroformyloxyphenyl) propane (66 g.,  $59^{\circ}/_{0}$ ) m.p. 89–90°C. (YAKUBOVICH<sup>18)</sup> quotes 87–88°C.).

# (g) Carbonate esters of 2-phenyl propan-2-ol

The appropriate chloroformate in ether was added dropwise to a stirred suspension of sodium 2-phenyl propan-2-oxide in ether during 90 min. After a further 30 min. water was added and the organic layer worked up to give the carbonate ester.

(i) Methyl. Colourless oil (94%), distilled at 80°C./10<sup>-6</sup> mm. to give an oil

 $n_{\rm D}^{20}$  1.5612,  $v_{\rm max}$  (C=O stretch) 1748, 1770 cm<sup>-1</sup>.

(ii) Ethyl. Colourless crystals (98%) m.p. 50°C., crystallised from petrol (b.p. 40-60°C.) as shining platelets

(C<sub>18</sub>H<sub>20</sub>O<sub>3</sub> (284.3) Calcd. C 76.0 H 7.1 Found C 76.3 H 7.1)

m.p. 55°C.,  $v_{max}$  (C=O stretch) 1760, 1770 cm<sup>-1</sup>.

(iii) Phenyl. Colourless oil (75%), distilled at 10<sup>-6</sup> mm. to give prisms

(C<sub>22</sub>H<sub>20</sub>O<sub>3</sub> (332.4) Calcd. C 79.5 H 6.1 Found C 79.5 H 6.0)

m.p. 58°C.,  $v_{max}$  (C=O stretch) 1778 cm<sup>-1</sup>.

# (h) Di(2-phenylprop-2-yl) carbonate (I)

(i) 2-Phenylpropan-2-ol (17 g.) and diphenyl carbonate (9 g.) were refluxed for 1 hr. and free phenol was then removed under vacuum. Crystallisation of the residue from *n*-butanol gave the ester (11 g., 61%) m.p. 108°C., recrystallised from ethanol as needles

(C<sub>31</sub>H<sub>30</sub>O<sub>3</sub> (450.6) Calcd. C 82.6 H 6.7 Found C 82.2 H 6.8)

m.p. 108°C.,  $\nu_{max}$  (C=O stretch) 1769, 1777 cm<sup>-1</sup>.

(ii) Phosgene (5% excess) in toluene (75 ml.) was added to sodium 2-phenylpropan-2 oxide (10 g.) in toluene (200 ml.) during 2 hrs. Working up yielded the ester (7.5 g., 78%) m.p. 108 °C.

## (i) Carbonate esters of bis(4-hydroxyphenyl)-2,2-propane

Prepared from the disodium salt of bis(4-hydroxyphenyl)-2,2-propane as described under (g).

(i) Methyl. Colourless crystals (91%) m.p. 89-91°C., recrystallised from methanol as colourless plates

 $(C_{19}H_{20}O_6 (344.4) Calcd. C 66.3 H 5.9 Found C 66.2 H 6.1)$ 

m.p. 91.5°C., v<sub>max</sub> (C=O stretch) 1762, 1767 cm<sup>-1</sup>.

(ii) Ethyl. Viscous oil (46%)  $n_D^{18}$  1.5353, distilled at 150°C./10<sup>-6</sup> mm. to give a colourless oil

> (C<sub>21</sub>H<sub>24</sub>O<sub>6</sub> (372.4) Calcd. C 67.7 H 6.5 Found C 67.9 H 6.5)

 $n_{\rm D}^{20}$  1.5362 v<sub>max</sub> (C=O stretch) 1764 cm<sup>-1</sup>.

(iii) Phenyl. Solid (80%) m.p. 92-93°C., recrystallised from methanol and from petrol (b.p. 40-60°C.) as needles

(C<sub>29</sub>H<sub>24</sub>O<sub>6</sub> (468.5) Calcd. C 74.3 H 5.2 Found C 74.5 H 5.1)

m.p. 101–102°C.,  $\nu_{max}$  (C=O stretch) 1766, 1781 cm<sup>-1</sup>.

# (j) Bis {[2(4-oxyphenyl)-2-phenyl propane] carbonyl}-4,4'-dioxy (diphenyl-2,2-propane) (II)

2,2-Bis(4-chloroformyloxyphenyl) propane (7.54 g.) and sodium 2-phenylpropan-2oxide (10 g.) were mixed, treated with dry ether (150 ml.) and stirred for 4 hrs.; the solution was then washed, dried, and concentrated. Treatment of the residue with methanol gave, with difficulty, colourless crystals (8.3 g., 55%) m.p. 118 °C. Recrystallisation from *n*-propanol yielded the ester (II)

m.p. 125 °C.  $\nu_{max}$  (C=O stretch) 1773, 1783 cm<sup>-1</sup>. This compound was recovered unchanged after heating for 5 hrs. at 300 °C./10<sup>-6</sup> mm.

#### 2.2 Irradiation

The purified compounds were placed in glass ampoules equipped with break seals and rigorously degassed by melting under vacuum  $(10^{-6} \text{ mm.})$ ; the ampoules were then sealed. The ampoules, cooled externally by a water-spray, were exposed to a linear accelerator electron beam (4 m.e.V.) at a dose rate of 1.04 megarads/min.

## 2.3 Analysis of Products of Irradiation

Gaseous products were analysed by mass spectroscopy. Solid and liquid products were examined by vapour phase chromatography and by infrared and ultraviolet spectroscopy.

## 3. Results

## 3.1 Gaseous Products of Irradiation

The mass spectroscopic analyses of the quantities (ml./g.) of gases evolved on irradiation of model compounds and polymer to a dose of 1000 megarads are given in Table 1.

Gas	Compound				
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	$C_6H_5\dot{C}O_3C_6H_5$	HRCO <sub>3</sub> RH *)	HRCO3RCO3RH *)	(RCO <sub>3</sub> ) <sub>n</sub> *)
Carbon monoxide	0.032	11.76	7.41	5.40	8.50
Carbon dioxide	0.019	2.85	2.14	1.78	4.53
Hydrogen	0.646	0.07	0.32	0.21	0.31
Methane	0.170		0.034	0.03	0.029
Benzene	0.059	0.16	<u> </u>	0.008	_
Ethylene	0.015	_	_	-	
Acetylene	0.015			·	_
Propylene	0.010	-		-	-
Butane	0.006		_	-	—
Ethane	0.004	_	_	_	
Toluene	0.002	_		_	_
Oxygen	—	-	—	0.046	



## 3.2 Solid and Liquid Products of Irradiation

## (a) 2,2-Diphenyl propane

Little change was observed in the vapour phase chromatogram of this compound after a radiation dose of 1000 megarads.

## (b) Diphenyl carbonate

Infrared analysis of the irradiated (1000 megarads) compound showed the formation of fresh absorption bands  $v_{max}$  3609, 3559, 3490 (O-H stretch), 1696, 1614, 1606 (C=O) and 1264 (C-O) cm<sup>-1</sup>. The ultraviolet spectrum in chloroform showed a single absorption band  $\lambda_{max}$  311 mµ,  $E_{1\%}^{1}$  9.73 tailing into the visible region and responsible for the pale amber colour of the irradiated material. Vapour phase chromatography followed by infrared analysis revealed the following components in order of increasing retention time: phenol, diphenyl ether, o-hydroxy diphenyl ether, diphenyl carbonate and two minor constituents both exhibiting OH and CO absorption bands (compounds possibly formed by interaction of phenoxy radicals with diphenyl carbonate). The identity of the compounds isolated was established by comparison of retention times, infrared spectra and melting points with those of authentic specimens.

## (c) Model carbonate (I)

Infrared analysis showed the formation of OH groups but little other identifiable change. The ultraviolet spectrum in chloroform showed a single absorption band  $\lambda_{max}$  306 mµ,  $E_{1\%}^{1 \text{ cm}}$  8.09.

### 4. Discussion

Consideration of the structure of poly[2,2-propane-bis(4-phenyl)carbonate] (III) and of earlier evidence<sup>3,5)</sup> shows that degradation



under the influence of ionising radiation is most likely to occur at the *iso*-propylidene and carbonate linkages. Benzene rings are highly resistant to breakdown both in simple compounds<sup>19</sup>) and in polymers<sup>20, 21</sup>) and attack at these points in the chain is unlikely to result in chain scission.

From the mass spectroscopic analyses it is apparent that the breakdown of 2,2-diphenyl propane gives primarily hydrogen and methane and that these gases are also evolved from the polymer and model compounds (I and II) in proportionately smaller quantities. The low yield of hydrogen from the breakdown of diphenyl carbonate and the relatively small amounts of hydrogen and methane evolved from the polymer indicate that the *iso*propylidene group is not an important source of weakness in the polymer chain.

The carbonate linkage, however, undergoes considerable degradation on irradiation as is evident from the high yields of carbon monoxide and carbon dioxide both from the model compounds and from the polymer. The various products isolated from the breakdown of diphenyl carbonate can readily be explained by the following scheme:



It is apparent from the high  $CO/CO_2$  ratio that reaction 1 is favoured and the results suggest that breakdown of PhOCO• to the phenoxy radical occurs in preference to breakdown to the phenyl radical. The instability of the PhOCO• radical is analogous to that of  $CH_3OCO•$  which is a probable intermediate in the photolysis of methyl carbonate<sup>8</sup>).

The formation of benzene and phenol arise from hydrogen abstraction reactions of the phenyl and phenoxy radicals. The occurrence of the FRANCK-RABINOWITCH cage effect in the crystal lattice readily explains the formation of diphenyl ether and *o*-hydroxy diphenyl ether by the recombination reactions:

$$\bigcirc -0C00\bullet + \bullet \bigcirc \rightarrow \bigcirc -0\bullet + \bullet \bigcirc + C0_2 \rightarrow \bigcirc -0- \bigcirc + C0_2$$
  
HO  
HO  
$$\bigcirc -0C0\bullet + \bullet 0- \bigcirc + \bullet 0- \bigcirc + C0 \rightarrow \bigcirc -0- \bigcirc + C0$$

The second scheme bears a resemblance to the photochemical rearrangement of aryl benzoates to *o*-hydroxy benzophenones described by KOBSA<sup>22</sup>).

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The absence of diphenyl from the products again indicates that decomposition of PhOCO• to a phenyl radical does not normally occur.

Although the solid products of degradation of the model compounds I and II were not analysed in detail the close parallels between the gaseous products and the changes in infrared spectra of these and of those of diphenyl carbonate indicate a similar pattern of reactions in these cases.

It is likely that operation of a cage effect in the polymer, analogous to that occurring in diphenyl carbonate, is responsible for the low G (scission) value (0.09) observed previously<sup>5</sup>) since, in the present instance, G (CO +  $CO_2$ ) is approximately 0.57 indicating that a much greater rate of scission should occur in the absence of radical recombination reactions. The results obtained are in agreement with the electron spin resonance studies of BARKER<sup>4</sup>) which showed that G (radicals) was approximately twice the value of G (total gas), but, as expected, these values are much greater than the G (scission) value<sup>5</sup>). The increased formation of hydroxyl groups<sup>3</sup>) and increases in the  $CO_2/CO$  ratio and G (scission) value<sup>5</sup>) observed on irradiation of the polymer in oxygen are evidence of the combination of free radicals with oxygen which reduces the degree of recombination.

The results of the present work show that the carbonate linkages in the polycarbonate molecule are very susceptible to degradation and suggest that the cage effect, which gives rise to radical recombination reactions, is a very important factor in reducing the rate of chain scission and tends to increase the radiation stability of the polymer.

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