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Flash Photochemical Studies of Polycarbonate and Related Model Compounds, Photodegradation vs. Photo-Fries Rearrangement^{1a,b}

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ABSTRACT: Quantum yields for the production of transient aryloxyl radical and formation of salicylate rearrangement or phenolic products have been measured in flash photochemical studies of polycarbonate and related model compounds in deaerated 1,2-dichloroethane solutions. The 3-µsec transient absorption and final product spectra of the polymer system were essentially identical with the spectra recorded with $bis(4-\alpha$ -cumylphenyl) carbonate. There was no effect on the initial M_n , M_w/M_n , or the presence of uncapped phenol end groups upon the spectra. However, based on gel permeation chromatography results, the quantum yield of chain breaking in the polymer system is significantly higher (0.11 $\leq \phi < 0.22$) than the quantum yield of aryloxyl (0.085) or phenolic products (0.080). Thus a spectroscopically unobservable chain scission process occurs with an efficiency approaching that due to carbonate group scissioning and is almost as efficient as the intramolecular Fries rearrangement which forms salicylates (0.18). In sum, the photodegradative chain-breaking reactions are as efficient as the nonscissioning rearrangement process. The extraneous chain-breaking process in the polymer system is thought to be initiated by abstraction of a hydrogen atom from a methyl group of the polycarbonate chain.

The ultraviolet (uv)-promoted reactions of poly(arvl esters) and related model compounds^{3a-6} have been of interest to polymer photochemists because mechanistic studies of primary photophysical and photochemical processes^{7,8} offer the possibility that new approaches to photostabilization of the polymer systems can be identified. In fact, exploitation of uv-promoted reactions in poly(aryl ester) coating materials for protection of otherwise photodegradable plastic substrates has been described.⁹ In this paper flash photolysis investigations of the primary photochemical reactions of poly(aryl carbonate esters) derived from bis(phenol A) (2,2-bis(4-hydroxyphenyl)propane, VIIIa. often noted as BPA or dian) and of related model compounds are described. The results are relevant to earlier proposals regarding the overall mechanism of these reactions^{1a} and bear directly upon the question of the uv sensitivity of BPA-polycarbonate,¹⁰⁻¹³ a commercially important thermoplastic material.¹⁴

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- (2) (a) General Electric Corporate Research and Development, Schenectady, N. Y. 12301. (b) General Electric Co., Mount Vernon, Ind. 47620.
- (3) (a) M. Okawara, S. Tani, and E. Imoto, Kogyo Kagaku Zasshi, 68, 223 (1965); Chem. Abstr., 63, 3068g (1965). (b) S. B. Maerov, J. Polym. ci., Part A, 3, 487 (1965).
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- (5) D. Belluš, Z. Maňásek, P. Hrdlovič, and P. Sláma, J. Polym. Sci., Part C, 16, 267 (1967). (6) D. Belluš, Z. Maňásek, P. Hrdlovič, P. Sláma, and Ľ. Ďurišinová, J.
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Under photochemical conditions diarvl carbonate. ArO-C(O)OAr, and poly(aryl carbonate esters) yield products similar to those found in the photoreactions of aryl esters, ArOC(0)R, and poly(aryl esters).^{8,15} This suggests a common mechanism and implies a correspondence between the primary stages of the photoreactions of the carbonate and carboxylate esters. Fries-type rearrangement products and the corresponding hydroxyaromatic compound usually account for the major portion of the consumed ester reactant under a variety of conditions.^{8,15} For example, uv irradiation of bis(4-tert-butylphenyl) carbonate (I) in alcoholic solution (Scheme I) produces ortho-Fries product II





(a salicylate derivative), the dihydroxybenzophenone III, 4-tert-butylphenol IVa, and intractable material. Under

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·OAr



c. $R = -OCH_2 C_6 H_5$

steady illumination conditions the sequential photochemical rearrangement of $I \rightarrow II \rightarrow III$ accounts for the formation of the latter and the low yield of II.^{12,16} Under flash photochemical conditions, however, the secondary process is obviated.

The nature and distribution of the products in these reactions clearly indicate that radicals are intermediates at some point in the initial stages of the reactions. In a recent review of the photochemical Fries rearrangement process Belluš concluded that two parallel primary processes occur in aryl esters:⁸ path A, the direct photolytic dissociation of the first ester excited state to form caged aryloxyl and acyl radicals,17 from a high-energy state, and path B, a concerted intramolecular 1,3 or 1,5 shift of an acyl group,¹⁸ from an energetically lower electronic level.



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Recently, we reported^{1a} that oligomeric cyclic BPA-carbonate esters V, rearrange via two intermediates (VIa,b) to the corresponding ortho-Fries product without the concomitant formation of flash photolytically detectable concentrations of aryloxyl radicals (10-µsec time scale). On the other hand, acyclic analogs I, VIIa, and VIIIb of otherwise essentially equivalent chromophoric character showed considerable transient aryloxyl absorption in the 400-nm absorption region and yielded other products as well as the ortho-Fries derivatives. These results were interpreted by two different photophysical paths in agreement with the analysis of Belluš but implied a reversal of the presumed energy levels involved in the two processes. Reactions 1-4 detail the first steps in the proposed scheme for *p*-alkyl-substituted phenyl carbonate esters.

Excitation

$$\operatorname{Ar'OC}(O)\operatorname{OAr} + h\nu \ (\lambda < ca. 284 \text{ nm}) \rightarrow$$

 $\operatorname{Ar'OC}(O)(\operatorname{OAr})^*$ (1)

Concerted rearrangement

$$E_1 \rightarrow VIa \rightarrow VIb \rightarrow e$$
-hydroxyketone derivative (e.g., II) (2)

Intramolecular radiationless energy transfer

 \mathbf{E}_{1}

Homolysis

$$E_2 \text{ or } E_3 \rightarrow [Ar'OC(O) \cdot OAr]$$
 (4)

The proposed scheme^{1a} followed from the observation that the only readily identifiable difference between the acyclic and cyclic carbonate esters was the difference in the conformational lability of the carbonyl moiety between the phenolate groups. Models of the cyclic esters indicated that the carbonyl groups cannot rotate freely in the cis-trans (ct) configuration (IXb) strictly imposed in the cyclic structure; it is held nearly perpendicular to the plane of both phenyl groups. The carbonyl carbon is fixed perfectly for backside bond formation with the ortho carbons of the aromatic system attached at the cis juncture. In contrast, facile interconversion between the ct and tt species is possible in models of the acyclic esters (5).



Rotation of the phenyl ring about the aromatic carbon ester oxygen bond in the cis conformers involves a very strong steric interaction of the ortho hydrogens with the nonbonding n orbitals of the other ester oxygen. There is what appears to be a relatively minor steric interaction of the ortho hydrogens with the carbonyl oxygen as the phenyl group is rotated about the aromatic carbon-ester oxygen bond in the trans configuration.¹⁹ Thus if there are any symmetry restrictions upon the efficiency of the radiationless energy transfer process (3), there is a less severe restriction for π -orbital interactions or achievement

⁽¹⁹⁾ A. E. Tonelli, Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem., 13, 1023 (1972).

 Table I

 Intrinsic Viscosity and GPC Data for Unexposed and Flashed

 (-f) Polymer Samples

	[η] ₀ , dl/g				GPC ^b	
Sample	<i>p-</i> Dioxane	CH ₂ Cl ₂	Cl₂Et	${10^{-3}\over M_{ m w}{}^a}$	$\frac{10^{-3}}{M_{\rm w}}$	$\frac{10^{-3}}{M_{\rm n}}$
Co	0.56	0.49	0.51	31.6	31.8	12.3
Co-f					23.6	9.7
C_1	0.57	0.51	0.53	32.5	32.2	17.3
C1-f					25.8	13.1
C_2	0.64	0.58	0.57	38.7	39.2	25.0
C ₂ -f					29.4	16.6
U	0.65	0.53	0.57	39.7	34.9	16.9
U-f					27.9	11.8

 $^aM_{\rm w}$ calculated from intrinsic viscosity in *p*-dioxane according to eq 6. ^b See text concerning GPC calibration conversions from polystyrene to capped, uncapped, and flashed polycarbonates.

of a satisfactory alignment of transition dipoles in the trans conformers.

The initial radiatively populated excited state E_1 in these esters is a $1\pi^*$ state of the phenolate group.^{la} Therefore within the framework of this scheme the carbonate esters are to be considered bichromophoric. Equilibrium 5 is probably attained during the lifetime of E_1 , and except in the cyclic esters, E_1 either undergoes a concerted intramolecular cyclization to an oxocyclohexadienyl radical (VIa in reaction 2) via cis conformations or participates in a conformationally sensitive radiationless energy transfer process (3) with the carbonyl π system (presumably only in trans conformations) to produce E_2 . Caged radical pairs are formed from E_2 or possibly some lower energy state E_3 ; these processes are discussed below.

Incursion of the path A homolysis process (4) in the polymer systems would lead to molecular weight changes which would reflect the proportion of geminate radicals which (a) reacted irreversibly with (residual) oxygen or abstracted hydrogens to yield stable chain breaks, i.e., degradation, and (b) the fraction of kinetically free radicals which couple to re-form the chain with rearranged backbone groups, *i.e.*, redistribution. Path B intramolecular rearrangement process (2) should result in no degradation or redistribution. Thus comparisons of flash photolysis studies of the polycarbonate and related model compounds with a concommitant study of the molecular weight changes in the polymer systems were made to assess the relative importance of these steps in the mechanism of the photoreactivity of arvl ester chromophores^{1a,8} and the photodegradation of the polymer systems.¹⁰⁻¹³

Experimental Section

Materials and Sample Preparations. Two samples of Lexan (General Electric Co.) polycarbonate resin were used; neither sample contained any additives. Sample U was an uncapped powdered resin whereas sample C_0 had been chain terminated with a monohydric phenol to yield a powdered resin with a residual phenol end-group content corresponding to less than 10% theoretical. The uncapped phenol end groups were not detectable by uv absorption spectroscopy. Gel permeation chromatographic (GPC) and intrinsic viscosity data for these samples after drying in vacuo at 80⁶ are shown in Table I.

To assess the effects of initial molecular weight and molecular weight distributions upon the photoreactions of BPA-polycarbonate, the C_0 resin was fractionated. Part of the C_0 resin was precipitated from dilute solution in spectroquality dichloromethane by titration with reagent grade methyl ethyl ketone. A portion of the precipitated powder was subjected again to the same procedure to further reduce the low molecular weight fraction of the capped sample. Table I presents the GPC and intrinsic viscosity data for the dried samples C_1 and C_2 .

Spectroquality 1,2-dichloroethane (Cl₂Et) was used to prepare

Polycarbonates, and Related Compounds ^a				
Sample or Compound	$\lambda_{\max} (nm)^b$	εw (ml/ (mg cm))	$\epsilon_{M}(l./(mol \ cm))$	
I	(282)			
	269.5	1.96	639	
	262	2.30	750	
IVa	(294)			
	285	1.20	1800	
	278	1.40	2100	
V(n = 3)	(286)			
	271.5	3.46	2640	
	264.5	3.84	2 9 30	
V(n = 4)	(286)			
	271.5	3.42	3480	
	265	3.89	3950	
VIIa	(283)			
	270	2.73	1290	
	263.5	3.34	1580	
VIIb	(292)			
	284	7.25	3500	
	277	8.85	4280	
VIIIb	(286)			
	270	2.49	1480	
	263.5	3.06	1810	
VIIIe	(297)			
	284	7.90	1680	
	278	9.23	1970	
Co	(283)			
	271.5	3.11		
	265	3.58		
Cı	(283)			
	271.5	3.43		
	265	3.96		
С2	(283)			
	272	3.42		
	265.5	3.93		
U	(290)			
	283.5°	0.16		
	272	3.52		
	265.5	3.97		

^a Cary 14 uv spectra. ^b Values in parentheses refer to onset of absorption. ^c Shoulder absorption due to phenolic end groups.

0.87 (±0.01) mg/ml stock solutions of the polymer samples. The fraction of the flash energy in the 200- to 280-nm region absorbed by each sample during the flash photolysis experiments was thus about the same (compare the ϵ_w values in Table II).

Ultraviolet absorption spectra (1-cm cells) of the C resin samples in Cl_2Et were essentially the same in the 260- to 280-nm region. Extinction coefficients are tabulated in Table II. The small difference in the ϵ values for C_0 and $C_{1,2}$ is within the error limits associated with the absorbancy measurements with only a single sample concentration. Adherence to Beer-Lambert behavior was demonstrated previously.²⁰ The uv spectral data also indicated that while fractional precipitation of the C resin removed low molecular weight species from the distribution, it did not remove chromophoric impurities which contribute to the very low level tailing absorption observed between *ca*. 285 and 330 nm (*ca*. 0.02 and 0.00₅ absorbance units, respectively, in the spectra).

Commercial samples of I were recrystallized twice. The cyclic esters V have been described previously.^{1a}

Bis[4- $(\alpha, \alpha$ -dimethylbenzyl)phenyl) Carbonate [or Bis(4- α cumylphenyl) Carbonate] (VIIa). To a stirred solution of 4- $(\alpha, \alpha$ -dimethylbenzyl)phenyl chloroformate (4.3 g, 0.015 mol) in pyridine (30 ml) was added water (2 drops), resulting in an exothermic reaction. After stirring for 30 min the crude carbonate was precipitated from solution by addition to hydrochloric acid (360 ml, 1 N). Extraction of the waxy solid into chloroform was followed by washing with dilute hydrochloric acid and water and

(20) R. S. Roller, unpublished data.

Table II Ultraviolet Absorption Characteristics of Diaryl Carbonates, Polycarbonates, and Related Compounds^a

by vacuum stripping to dryness. Compound VIIa was obtained as fine needles from methanol, mp 108-110°. The spectral data were: ir (KBr disk), 1773 (C=O), 1250 cm⁻¹ (C-O); pmr (CCl₄) δ 1.70 (CH₃, 6), 7.25 (aromatic region, 9).

Bis(4-tert)**butylphenylCarbonate of VIIIa** (VIIIb). To a stirred solution of the bis(chloroformate) of VIIIa (8.82 g, 0.025 mol) in dichloromethane (100 ml) was added dropwise a solution of 4-tert-butylphenol (8.25 g, 0.055 mol) and pyridine (6.0 g, 0.075 mol) in dichloromethane (50 ml). After stirring for 30 min the solution was extracted with dilute hydrochloric acid (100 ml, 0.25 N), twice with an equal volume of water and dried over silica gel. The residue from concentration of the dried dichloromethane on the steam bath was crystallized from methanol and then recrystallized twice from heptane giving VIIIb (5.4 g) as plates, mp 115–118°. The spectral data were: ir (KBr disk) 1770 (C=O), 1250 cm⁻¹ (C-O); pmr (CDCl₃) δ 1.33 (C(CH₃)₃, 18), 1.70 (>C(CH₃)₂, 6), 7.1-7.6 (aromatic region, 16).

Bis(phenyl carbonate) of VIIIa (VIIIc). To a stirred solution of VIIIa (5.7 g, 0.025 mol) and pyridine (6.0 g, 0.075 mol) in dichloromethane (100 ml) was added a solution of phenyl chloroformate (7.8 g, 0.05 mol) in dichloromethane (50 ml). After 30 min the system was worked up as for VIIIb. The crystalline residue obtained after removal of the dichloromethane was recrystallized twice from methanol and finally from *n*-hexane, giving VIIIc (3.5 g), mp 101-102°. The spectral data were: ir (KBr disk) 1774 (C=O), 1230 cm⁻¹ (C-O); pmr (CDCl₃ δ 1.70 (>C(CH₃)₂, 6), 7.15-7.60 (aromatic region, 18).

Monobenzyl Ether of VIIIa (VIIIb). Compound VIIIa (68.49 g, 0.3 mol) was dissolved in a solution of sodium hydroxide (24.3 g, 0.608 mol) in water (2250 ml). To the resultant solution, heated to 75°, benzyl chloride (37.95 g, 0.3 mol) was added over 15 min with vigorous stirring. Following 2.5-hr refluxing the system deposited a tan granular solid on cooling which was filtered and washed with water and dried. Compound VIIIg (72 g, 75% yield) was recrystallized from benzene-heptane-cyclohexane, mp 105-106.5°. Repeated recrystallization raised the melting point to 107-108°. The spectral data were: ir (KBr disk) 3330 (OH), 738 and 692 cm⁻¹ (monosubstituted aromatic); pmr (CDCl₃) δ 1.63 (>C(CH₃)₂, 6), 5.0 (>CH₂, 2), 6.4-7.4 (aromatic region, 13). Anal. Calcd for C₂₂H₂₂O₂: C, 82.98; H, 6.96. Found: C, 83.01; H, 6.94.

Acetylation of VIIIg with acetic anhydride-concentrated sulfuric acid gave VIIIg acetate, mp 68-71° from aqueous methanol. The ir spectrum (CS₂ solution) showed no -OH absorption but a C=O absorption at 1770 cm⁻¹. Anal. Calcd for C₂₄H₂₄O₃: C, 79.97; H, 6.71. Found: C, 79.86; H, 6.59.

Bis[4-(4-benzyloxy- α , α -dimethylbenzyl)phenyl] Carbonate (VIIc). Compound VIIIg (9.1 g, 0.028 mol) was dissolved in pyridine (100 ml) and treated with phosgene for 8 min at a flow rate of 0.38 g/min (0.0307 mol, ~100% excess). The cooled solution was treated with dilute hydrochloric acid and the resultant mixture was extracted with dichloromethane. After drying over calcium chloride the solvent was evaporated to give crude VIIc (7.0 g). Exhaustive recrystallization from acetone-methanol gave a product which coalesced at 115°, forming a clear melt at 122–123°. The spectral data were: ir (CS₂ solution) 1776 (C=O), 728 and 692 cm⁻¹ (monosubstituted aromatic); pmr (CDCl₃) δ 1.66 (>C(CH₃)₂, 12), 5.06 (CH₂, 5), 6.93–7.44 (aromatic region, 26). Anal. Calcd for C₄₅H₄₂O₅: C, 81.53; H, 6.38. Found: C, 81.25; H, 6.25.

Bis[4-(4-hydroxy- α, α -dimethylbenzyl)phenyl] Carbonate (VIIb). Compound VIIc (20 g, 0.030 mol) in ethyl acetate solution was shaken with hydrogen at 20° and 10-in. water pressure in the presence of freshly prepared 20% palladium on charcoal (2.0 g) until hydrogen uptake ceased. After separation and washing of the catalyst the combined liquid phase was concentrated under vacuum giving crude VIIb (11.8 g, 81.5%), mp 168-70° (from dichloromethane-hexane). Further recrystallization from benzene and ethyl acetate-hexane raised the melting point to 172-172.5°. Spectral data were as follows: ir (KBr disk) 3518 and 3455 (OH), 1763 (C=O), 1260 cm⁻¹ (-C-O); pmr (CDCl₃) δ 1.66 (>C(CH₃)₂, 12), 6.76-7.25 (aromatic region, 16).

Bis(2,6-xylyl) Carbonate (X). Phosgene (14.5 g, 0.146 mol) was passed into a gently refluxing, stirred solution of 2,6-xylenol (35.8 g, 0.293 mol) in pyridine (100 ml) over 21 min. The crude product, isolated on pouring the cooled reaction mixture in water, was taken up in methylene chloride (200 ml) and the organic phase was washed with dilute hydrochloric acid until pyridine free. Following water washing and drying over calcium sulfate, the solvent was removed and the residue was crystallized first from aqueous methanol and then from aqueous acetic acid to give X (25 g) in



Figure 1. Transmission of a 5 mm thickness of a saturated nickel(II) and cobalt(II) sulfate solution used to filter the high-intensity photolysis flash.

fine needles. Spectral data were as follows: ir (KBr disk) 1773 (C=O), 1250 cm⁻¹ (C-O); pmr (CCl₄) δ 2.3 (CH₃, 6), 7.05 (aromatic region, 3).



4-(4-Benzyloxy- α,α -dimethylbenzyl)phenyl Phenyl Carbonate (VIIIh). Compound VIIIg (31.8 g, 0.1 mol) and phenyl chloroformate (15.6 g, 0.1 mol) were heated together in refluxing pyridine for 4 hr. The cooled reaction mixture was poured into water and worked up in the usual way. Crude VIIIh (26.9 g) was obtained from 95% ethanol, mp 85-87°. Successive recrystallization from hexane and methanol raised this to 87.5-89.5°. Spectral data were as follows: ir (CS₂ solution) 1770 cm⁻¹ (C==O); pmr (CDCl₃) δ 1.66 (>C(CH₃)₂, 6), 5.07 (>CH₂, 1.9), 6.93-7.44 (aromatic region, 18.4). Anal. Calcd for C₂₉H₂₆O₄: C, 79.43; H, 5.97. Found: C, 79.53; H, 6.34.

4-(4-Hydroxy- α,α -dimethylbenzyl)phenyl Phenyl Carbonate (VIIId). Compound VIIIh (50 g, 0.11 mol) in ethyl acetate (400 ml) was shaken with hydrogen in the presence of 5% palladium on charcoal (20 g) at an initial pressure of 50 psi. The uptake of hydrogen was complete in 3 hr. Isolation in the usual way and crystallization from cyclohexane gave crude VIIId, mp 78-83°. Recrystallization from benzene raised the melting point to 88-89.5° (lit. mp 85°).²¹ Spectral data were as follows: ir (CS₂ solution) 3510 (OH) and 1789 cm⁻¹ (C=O). Anal. Calcd for C₂₂H₂₀O₄: C, 75.84; H, 5.87. Found: C, 76.0; H, 5.94.

Flash Photolysis Apparatus. The unit was of the typical coaxial type with two linear xenon flashlamps along the 12×1 cm diameter cylindrical quartz reaction vessel. The cell had an outer jacket filled with a saturated aqueous solution of nickel(II) and cobalt(II) sulfate. The effective path length for the filter solution was 5 mm; the transmission spectrum is shown in Figure 1. The ends of the cell were covered to eliminate stray light contributions from the photolysis flash to the exposure of the spectrographic plate. Thus only about 87% of the cell was irradiated directly.

The photolysis flash duration was about 25 μ sec (measured after 90% reduction of the peak intensity) and the monitoring flash had a half-time duration of 10 μ sec. Further details are in ref 1a and 22.

Delay times (est error $\pm 2 \ \mu sec$) were measured from oscillograms as differences between the peaks of the photolysis and monitoring flashes.

High-purity nitrogen was bubbled 5-10 min through the solutions in the reaction cell to reduce the oxygen content prior to ex-

- (21) U.S. Patent 3,549,682.
- (22) J. S. Humphrey and J. H. Fielding, Rev. Sci. Instrum., 41, 1584 (1970).



Figure 2. Transient absorption spectra of flash-photolyzed polycarbonate samples: $(---) C_0/3$ -µsec prefire (see Results); $(. . .) C_1/13$ -µsec delay; and 3-µsec delay spectra of U (----), C_0 (-O-O-), C_1 (-O-O-), and C_2 (- Δ - Δ -).

posure. Although oxygen plays a role in the photochemistry of the model compounds and polymer systems under steady irradiation conditions,^{1a,8} the results with the cyclic model compounds (V)^{1a} indicated that it plays no role in the rearrangement process under flash photochemical conditions.

After the flash photolysis experiment proper, the spectrum of the reaction mixture was recorded spectrographically about 1 min later in the same 12-cm cell. Final uv spectra of the reaction mixtures were recorded in 1- or 2.5-cm cells using a Cary 14 spectrophotometer.

Polymer Molecular Weight Measurements. Intrinsic viscosities of the original polycarbonate samples were determined at 25° in *p*-dioxane, dichloromethane, and Cl₂Et (Table I). The weightaverage molecular weights, M_w , were calculated from the η values in *p*-dioxane by the relation²³

$$[\eta]_0 = 6.0 \times 10^{-4} M_{\rm m}^{0.66} \tag{6}$$

and are shown in Table I (column 5).

GPC molecular weight and the molecular weight distribution determinations were made with a Waters Associates analytical gel permeation chromatograph. The five columns were packed with styrene-divinylbenzene beads having 10^6 , 10^5 , 10^4 , 10^3 , 10^2 Å nominal pore sizes. The polycarbonate samples were prepared from aliquots of the stock Cl_2Et polymer samples and of the flashed solutions; these were evaporated to dryness at room temperature under a slow stream of nitrogen. The dry polymers were dissolved in dichloromethane for the GPC analyses.

Narrow distribution polystyrene (PS) samples (Pressure Chemical Co.) and styrene monomer were used to calibrate the GPC columns for dichloromethane at room temperature. The calibration values were obtained from a semilogarithmic plot of M_w (PS) vs. the retention volume. To transform the GPC calibration by PS to GPC calibrations for the capped, uncapped, and flashed polycarbonates (PC) two conversions were necessary. First, for the original capped polycarbonates, values of M_w (PS) computed by integration of the GPC traces using the PS calibration were multiplied by a factor to give the M_w (PC) equal to those (Table I, column 5) computed from eq 6. For the capped polycarbonates $(C_{0,1,2})$ this required the calibration adjustment M_w (PC) = 0.50 $M_{\rm w}$ (PS). For the uncapped sample U and all flashed samples a second correction was necessary to compensate for the specific retention volume increase of molecular species having phenolic end groups. Low molecular weight carbonate esters VIIb, VIIId, and VIIIc, having two, one, and zero phenolic groups, were passed through the GPC column and the retention volumes of their peak positions were noted in terms of the corresponding M_w (PS). Table III records the results.

From the GPC and $[\eta]_0$ data on doubly capped polycarbonate samples, the expected relationship is M_w (PC)/0.50 = $(M_w/0.50)$ - M_w (PS). This holds within 1.8% for the doubly capped VIIIc.

(23) A. R. Shultz, P. L. Wineman, and M. Kramer, Macromolecules, 1, 488 (1968).

 Table III

 Actual Mw, GPC-Determined Values Based on Polystyrene

 Calibration, and Expected Values Based on GPC-Mw

 Relationship for Model Compounds with Two, One, and Zero

 Phenolic End Groups

Compound	M _w	$M_{ m w}({ m PS})$ at Peak	$M_{ m w}/0.50$
VIIb	482.6	260	965
VIIId	348.4	404	697
VIIIc	468.5	920	937

For the singly capped VIIId: $M_w/0.50 = M_w$ (PS) + 293. For uncapped VIIb: $M_w/0.50 = M_w$ (PS) + 705. The calibration relation for doubly capped PC was adjusted to one for uncapped PC by averaging the increased retention volume effect per hydroxyl group observed for VIIb and VIIId. This yields $M_w(PC) = 0.50$ $(M_w(PS) + 650)$ for uncapped polycarbonate (hydroxyl group on both ends of the chain). In evaluating by GPC the M_w and M_n of the flashed samples it was assumed that the small chains have predominantly hydroxyl terminal groups and the calibration for uncapped polycarbonate was used.

The GPC chromatograms were traced with a Calma Corp. Model 580 XY digitizer. The digital data were then numerically integrated by computer to give the molecular weight averages of the samples.

Results

(A) Comparisons of Transient Absorption Spectra. (1) The transient absorption spectra recorded about 3 μ sec after flashing the polymer samples are shown in Figure 2. Considering the degree of uncertainty in the density measurements with the spectrographic plates (±0.03 unit),²² they are essentially identical. Thus the initial M_n , molecular weight distribution, and the presence of phenol end groups (sample U) have no pronounced effect upon the spectroscopically observable phenomena.

(2) Also shown in Figure 2 are spectra of the transient polymer species recorded by monitoring flashes which in one case peaked 3 μ sec prior to the maximum of the photolysis flash and in the other case was delayed 13 μ sec after peak excitation. There is a clear correspondence of both with the band shapes of the 3- μ sec delay spectra. All observable aryloxyl radicals are formed during the photolysis flash proper and the absorbance in the 400-nm region in the 3- μ sec delay spectra may be taken as representative of the total concentration of aryloxyl radicals produced flash photolytically.

(3) The 3- μ sec delay spectra of the transient polymer species can be superimposed on that of model VIIa (Figure 3). For comparisons of the flash photochemical behavior of I, V, VIIa, and VIIIb (*vide infra*), the calculations based on the spectroscopic data for VIIa hold also for the polymer samples if it is assumed that the extinction coefficients of the chromophores in polymeric species are equal to those for the chromophores in models II, VIIIe, and VIIIf.

(4) (a) When dilute Cl₂Et solutions of phenols IVa or VIIIe are flashed under similar circumstances (*i.e.*, same initial per cent absorption and flashing conditions) the absorbance at the 420-nm absorption maximum of the 4- α -cumylphenoxyl radical VIIIf is about 5% greater than that at the 406-nm maximum of the 4-*tert*-butylphenoxyl radical IVb. Assuming a molar extinction coefficient of 1800 M^{-1} cm⁻¹ for the latter,²⁴ a value of 1900 M^{-1} cm⁻¹ is taken for VIIIf in all subsequent calculations.

(b) The transient spectrum in the 350- to 450-nm region recorded in the flash photolysis of VIIb (Figure 3) is a replica of that recorded for the radical VIIIf generated flash

(24) E. J. Land, Progr. Reaction Kinet., 3, 379 (1968).



Figure 3. Transient absorption spectra of model compounds: (---) VIIb/3-µsec delay; (---) VIIa/3-µsec delay; (---) VIIb/3-µsec delay.



Figure 4. Absorption spectrum of reaction mixture about 1 min after flash photolysis: (--) VIIb; (-•) VIIa; (-0-) VIIIb; (--) U.

photolytically from the phenol VIIIe. This is further evidence that there is no interfering absorption in this spectral region of the 3- μ sec delay spectra and that the absorbance at the long-wavelength maximum represents ary-loxyl radical absorption only.

(5) The 3- μ sec delay spectra for the uncapped resin sample U and model VIIb show almost identical absorption in the 350- to 450-nm region (Figures 2 and 3). The extra absorption at wavelengths less than 350 nm in the spectrum of sample U arises from the additional intermediates (related structurally to VIa and -b) which form ohydroxyaryl groups in the polymer chain. The dominance of aryloxyl radical formation over carbonate group photoreactions in VIIb reflects the high quantum yield for aryloxyl radical production from the corresponding phenol in Cl_2Et ($\phi \simeq 0.5$)^{1a} and the dominance of light absorption by the phenol end groups. Comparison of the molar ex-



Figure 5. Absorption spectrum about 1 min after flash photolysis of the capped polycarbonate samples $C_{0,1,2}$ and model compound I (---).

tinction coefficients of VIIa and -b in Table II indicates that about 65% of the absorbed quanta would be apportioned initially to the terminal phenol groups of VIIb.

(6) Although previously reported,¹ the spectrum of the transient species generated from I has been repeated using solutions of the same initial per cent absorption and exposed under the same conditions as the other samples of this study. The observed absorbance at the 406-nm maximum of the aryloxyl radical IVb ($A_{406}^{IVb} = 0.7_0$) corresponds to a concentration of $3.2 \times 10^{-5} M$ (see section 4a above). Aliquots of known concentrations of IVa were added to the exposed sample of I. After correction for base-line absorption, integrated band intensities were measured by planimetry. Extrapolation through zero of a plot of the increase in the integrated band intensity in the 285-nm phenolic-absorption region of the product spectrum vs. the added amount yielded a value of 3.4×10^{-5} M for the concentration of IVa produced by the photolysis of I. These values indicate a 1:1 stoichiometry for transient aryloxyl radical and (monohydric) phenol production

(7) The transient absorption spectrum of VIIIb in the 400-nm region clearly shows the overlapping spectra of radicals IVb^{1a} and VIIIf (Figure 3).

(8) A 2.0×10^{-3} M solution of bis(2,6-xylyl) carbonate X in deaerated Cl₂Et was flash photolyzed under the same conditions and no transient absorption (*i.e.*, <0.05 absorbance unit) was observed between 290 and 450 nm. Under equivalent flashing conditions, 2,6-xylenol produces intense typical aryloxyl radical absorption bands in the 400- to 420-nm region as well as other transient absorption.

(B) Product Spectra. (1) The absorption spectra of the reaction mixtures in the 12-cm cell about 1 min after flashing are shown in Figures 4 and 5. The striking result is that all model compounds and polymer samples show similar absorption bands in the 360- to 420-nm region. The assignment of these absorptions is discussed below.

(2) Absorption maxima due to salicylate chromophores structurally analogous to II are seen at 320 nm in the spectra of the polymer samples (Figure 6). The absorption from 355 nm into the visible region has been observed with all uv-irradiated acyclic diaryl carbonate compounds.



Figure 6. Short-path-length absorption spectra of polymer samples $C_{0,1,2}$ (broken lines) after flash photolysis compared to initial absorption of C_0 (solid line). The slight differences in the product spectra are not significant.

Shoulder absorption at 285 nm in the spectra shown in Figure 6 is due to phenol-type chromophores.

(C) Quantum Yield Calculations. Table IV shows the concentrations of phenols, salicylate derivatives, and aryloxyl radicals produced in the flash photolysis of I and VIIa. Within the approximations outlined below, the data for VIIa also apply to the polymer samples.

The method of measuring the amount of light absorbed by the reactant under flash photochemical conditions has been described.^{1a} There is an estimated $\pm 25\%$ error in the accuracy of the method, but repetition of the prior experiments with I under different conditions led to the same quantum yields as reported previously.^{1a} At concentrations of 0.87 mg/ml the amount of light absorbed by the polymer samples and model compounds at wavelengths less than about 280 nm was 1.7×10^{-3} . Quantum yields are evaluated as $\phi = \text{mmol}$ of compound/meinstein *absorbed* by reactant.

Except for the aforementioned phenol-addition method to determine the concentration of IVa formed from I, the concentrations of phenols and salicylate derivatives were calculated from the absorbance values at 285 and 320 nm in the product spectra.

The molar extinction coefficient for II at 320 nm (5000 M^{-1} cm⁻¹)^{1a} was assumed to be characteristic of the salicylate chromophore in the polymer chain as well as the derivatives formed in the irradiation of the other model compounds. The true values for these species are not expected to differ by more than 10%. (Compare ϵ_m values of IVa and VIIIe in Table II.) An arbitrary (subtractive) correction corresponding to an absorbance measured from an approximate linear extrapolation of the tailing absorption at wavelengths greater than 350 nm was employed before calculating the salicylate concentrations based on the absorbance values at 320 nm.^{1a}

For calculations of the substituted phenol concentrations in compounds other than IVa the molar extinction coefficient of the monohydric model VIIIe was used (Table II).

The flash photolysis result with VIIIb allows a check of the $\phi(\text{ArO} \cdot)$ values for I \rightarrow IVb and VIIa \rightarrow VIIIf. The

Table IV Concentrations and Quantum Yields of Transient Aryloxyl Radicals and Stable Products Formed by Flash Photolysis of Diaryl Carbonates

Sample	Molar Conc n, × 10 ⁻⁵			Quantum Yields (ϕ)		
	ArO·	ArOH	Sala	Ar0.	ArOH	Sal^a
I	3.2 ^b	3.4 ^c	3.2	0.20 ^c	0.22	0.20 ^c
VIIa ^d V	1.4 ^e	1.2	2.7	0.085	0.080	0.1 ₈ 0.1 ₆ g

^a Salicylate derivative. ^b Radical IVb. ^c See Results, section A.6. ^d Applies for all polymer samples as noted in Results, section A.3. ^e Radical VIIIf. ^f See Results, section C. ^g Reference 1a.

observed absorbance at 406 nm for VIIIb \rightarrow (IVb + VIIIf) is A_{406} (VIIIb \rightarrow ArO·) = 0.45 (Figure 3). Calculation of the contribution of VIIIf to this observed value makes use of the $\phi(ArO \cdot)$ values of Table IV to estimate the probability of producing an aryloxyl radical from an excited inner phenolate chromophore (i.e., assuming it is essentially a 4- α -cumyl-substituted moiety): $\phi(\text{VIIa} \rightarrow \text{VIIIf})/$ $[\phi(\text{VIIa} \rightarrow \text{VIIIf}) + \phi(\text{I} \rightarrow \text{IVb}] = 0.3_0$. Assuming equal a priori probability for absorption of a photon by the end and inner phenolate groups and taking into account the fact that $A_{406}(\text{VIIIf})/A_{420}(\text{VIIIf}) = 0.6$ (Figure 3), we calculate $A_{406}(\text{VIIIb} \rightarrow \text{VIIIf}) = 0.4_5 (0.3/0.6) = 0.2_2$; by difference, $A_{406}(\text{VIIIb} \rightarrow \text{IVb}) = 0.2_3$. Another approach to deducing the latter value, not invoking the $\phi(ArO \cdot)$ values, agrees with this result. Assuming that the relative value of the $\epsilon_{\rm m}$'s for I and VIIa (Table II) gives the probability that either an end or an inner phenolate chromophore will be the initial excited state, $\epsilon_{\rm m}(I)/\epsilon_{\rm m}(VIIa) =$ 0.5. The probability that a single end group in VIIIb will be excited and yield IVb is 0.5/(0.5 + 1) = 0.33. The result in section A7 was that under exactly the same flashing conditions and initial absorbancy in the 270-nm region, $A_{406}(I \rightarrow IVb) = 0.7_0$. Since equal numbers of quanta were absorbed in the two experiments, but there was only a 33% chance that a tert-butyl-substituted end group was excited in VIIIb, the expected absorbance at 406 nm due to IVb in the latter experiment is $A_{406}(\text{VIIIb} \rightarrow \text{IVb})$ = $0.7_0 \times 0.33 = 0.2_1$. The agreement with the value calculated from the $\phi(ArO \cdot)$ values is excellent considering the approximations. This suggests that VIIIb, which contains two different chromophores both with respect to absorptivity and efficiency of aryloxyl radical formation, behaves photolytically as expected based on the results with I and VIIa if the reactivity of the initial excited phenolate moiety is indeed independent of the other aromatic ester group (see Discussion section).

The quantum yields for chain scission of the polycarbonates by flash photolysis of their solutions in Cl₂Et were calculated as follows: The number of chain scissions per original molecule is given by $S = (M_n^o/M_n^f) - 1.^{25}$ Since only 87% of the total solution was *exposed* to the flash, the number of chain scissions per original exposed molecule is S/0.87. The number of chain scissions is therefore s= $(254/M_n^o) \times (S/0.87)$, where 254 is the gram formula weight of the mer. Under the flash conditions and solution concentrations employed, 3.3×10^{-2} mmol of mer absorbed 1.7×10^{-3} meinstein of photons. The number of initial excited states formed per mer exposed is thus $n_e =$ $1.7 \times 10^{-3}/3.3 \times 10^{-2} = 5.2 \times 10^{-2}$. The quantum yield for chain scission is then given by $\phi_d = s/n_e$. The quan-

⁽²⁵⁾ F. A. Bovey, "The Effects of Ionizing Radiation on Natural and Synthetic High Polymers," Interscience, New York, N. Y., 1958, Chapter IV.

Table V Concentrations and Quantum Yields of Chain Scissions in Flash Photolyzed Polycarbonate

Sample	S^a	s ^b	$\phi_{\mathbf{d}}{}^c$
Co	0.268	0.0063	0.12
C_1	0.32_{1}	0.0054	0.10
C_2	0.506	0.0059	0.11
U	0.432	0.0075	0.14

 aS = chain scissions per original polymer molecule based on total sample. bs = chain scissions per exposed mer. $^c\phi_{\rm d}$ = chain scissions per initial excited state.

tities S, s, and ϕ_d for the four polycarbonate samples are shown in Table V.

The quantum yield for chain scission is thus found to be $\phi_{d}(av) = 0.11$ for the capped polycarbonates and 0.14 for the single uncapped polycarbonate sample. Although the latter value is slightly higher than the former, the difference scarcely exceeds the uncertainties in the determinations. The $M_{\rm w}$ of polymer U as calculated from the GPC data was less than its M_w calculated from its intrinsic viscosity in p-dioxane. If the GPC molecular weights for sample U were forced to correspond to the latter, its ϕ_d would be decreased approximately 15%. Of greater importance is the effect on the GPC-determined $M_{\rm n}$ due to our assumption (cf. polymer molecular weight measurements, Experimental Section) of hydroxyl-terminal groups on both ends of photolyzed polymer chains. If no correction were made for the increased retention volume due to hydroxyl end groups in the GPC evaluation of M_n^{f} (i.e., M_n of the flashed polymers) an average $\phi_d = 0.22$ would be calculated. The true value of ϕ_d lies somewhere between 0.11 and 0.22, but nearer to the former.

Discussion

Initial Stages in the Photoreactions of Aryl Esters. Recent studies of aryl esters²⁶⁻³² place continued emphasis on the Kobsa homolysis mechanism¹⁷ as the primary process in these systems. However, our results with the cyclic and acyclic diaryl carbonate esters and the fact that phenyl salicylate derivatives rearrange cleanly without concomitant formation of fragmentation products^{1a} point to the importance of an interaction between the phenolate and carbonyl groups which populates a lower energy excited state that leads to radical formation. This has been formulated as a conformationally sensitive radiationless energy transfer process (3) with equilibrium (5) being the controlling feature in determining the efficiency of process (3) in the carbonate esters. Further evidence for this comes from the results with bis(2,6-xylyl) carbonate ester X. Rearrangement to the ortho positions is blocked by the methyl groups and the carbonyl group is perpendicular to

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- (27) R. F. Reinish, H. R. Gloria, G. M. Androes, Preprint of Papers on "Photochemistry of Macromolecules," Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct, 1969.
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- (30) A. Davis and J. H. Golden, J. Chem. Soc., B, 425 (1968).
- (31) F. A. Carroll and G. S. Hammond, J. Amer. Chem. Soc., 94, 7152 (1972).
 (32) C. E. Kalmus and D. M. Hercules (Tetrahedron Lett., 1575 (1972))
- (32) C. E. Kalmus and D. M. Hercules (*Tetrahedron Lett.*, 1575 (1972)) report that flash photolysis of 2,6-dimethylphenyl acetate in either hexane or a perhalohydrocarbon solvent produces transient benzylic radical absorption and subsequently, high yields of 2-formyl-6-methylphenyl acetate. Although the uv absorption spectrum of the Cl₂Et solutions of X showed minor changes after flash photolysis, no products could be separated by tlc under conditions where products from the flash photolysis of other diaryl carbonate esters were detectable.

both phenolate groups in IXa or -b, the situation being directly analogous to that in the cyclic esters V.^{1a} No transient absorption was observed in the 290- to 450-nm region when X was flash photolyzed under conditions where 2,6-xylenoxyl radical would have been observed if processes (3) and (4) had occurred.³² This is in accord with the suggestion that process (3) is inefficient in the trans conformers when the carbonyl and aromatic π systems are essentially orthogonal.

As noted above, a correspondence between the primary processes in diaryl carbonate esters and aryl esters of carboxylic acids is to be expected. Rearrangement to ohydroxylaryl Fries derivatives must be a concerted, intramolecular process⁸ which involves two intermediates (VIa and -b).¹⁸ It proceeds from a $1\pi^*$ excited state which is localized on the phenolate portion of the molecule.³³

Quantum yields for formation of salicylate derivatives from I, V, VIIa, and the polymer samples are the same within experimental error (Table IV). This suggests that the concentration of cis conformers must be about the same in all these systems. In order to achieve the cyclic structures V at least two ct junctures must be present, but it appears that all junctures must be ct in order to allow any flexibility whatsoever of the rings.^{1a} The relative number of cis (n_c) to trans junctures (n_t) is unity for the latter case. In *dilute solutions* of polycarbonate the ct configuration is favored significantly in equilibrium (5).³⁴ For n_c/n_t to approach unity as in the cyclic esters, the equilibrium constant for (5), K_5 , in the acyclic ester case would have to be on the order of 10. From the data of Williams and Flory,³⁴ $K_5 = [ct]/[tt] \simeq 9$ in agreement with this estimate. Thus ct conformers of model VIIa must also dominate in the equilibrium (5). It should be noted that K_5 must also favor the ct conformers in model I.

Energy Transfer and Homolysis Steps. Excited state E_2 was identified previously as a ${}^{1}\pi^*$ excitation localized on the carbonyl group. However, the onset of absorption by diethyl carbonate ($\lambda_{\text{onset}}^{\text{neat}} < 220 \text{ nm}$)^{1a} corresponds to a much higher energy than the 0,0 bands of the long-wavelength ${}^{1}\pi\pi^*$ absorption of diaryl carbonate esters, which lies approximately at 35,000 cm⁻¹ (285 nm, Table II).

The same situation exists with respect to ethyl acetate³⁵ and phenyl acetate.²⁹ A singlet-singlet energy transfer between the initial $\pi\pi^*$ state localized on the aromatic group and the ${}^{1}n\pi^{*}$ state of the carbonyl would appear to be ruled out on the basis of the relative energy levels involved. However, to the extent that the n electrons of the ester oxygen are polarized toward the aromatic π system, the inductive effect of the oxygen, which increases the separation of the n and π^* carbonyl orbitals in simple alkyl analogs,³⁶ is reduced. Thus it is conceivable that the $n\pi^*$ carbonyl state is either isoenergetic or nearly so with the ${}^{1}\pi\pi^{*}$ aromatic transition.³⁷ The situation in any given aryl ester would represent a balance between specific medium effects upon the electronic transitions of the phenolate and ester carbonyl group and structural features of the reactant;³² this provides a basis for rationaliz-

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- (34) A. D. Williams and P. J. Flory, J. Polym. Sci., Part A2, 6, 1945 (1968).
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 (36) J. N. Murrell, "Theory of Electronic Spectra of Organic Molecules,"
- (36) J. N. Murrell, "Theory of Electronic Spectra of Organic Molecules," John Wiley, New York, N. Y., 1963, Chapter 8.
- (37) A. A. Scala and J. P. Colangelo (J. Chem. Soc., D, 1425 (1971)) report that various ethyl sec-alkyl carbonate esters have very low intensity maxima in the 260-280 nm which presumably must involve an $n\pi^*$ excitation since the compounds undergo photochemical type II elimination reactions.

ing the diverse photobehavior which is displayed by aryl esters as a group.^{8,15}

There is no direct spectroscopic evidence to indicate that the $1n\pi^*$ carbonyl absorption lies under the $1\pi\pi^*$ phenolate absorption band in the aryl carbonate esters, but the relative extinction coefficients would favor the latter state in absorption by at least two orders of magnitude.

Several energy transfer schemes³⁸ involving the singlet and triplet excited states localized either on the carbonyl or aromatic groups can be postulated. Since Fries rearrangement occurs from the $1\pi\pi^*$ aromatic excited state and it seems unlikely that the $3\pi\pi^*$ phenolate excited state is dissociative,²⁹ we focus on the carbonyl excited states as being the ones most likely involved in the homolysis reaction and assume that singlet-singlet energy transfer process (3) is possible.

If E_2 is indeed a ${}^{1}\pi^*$ carbonyl state populated *via* (3), direct α cleavage would produce an aryloxyl and aryloxy-carbonyl radical (7).

$$\begin{array}{ccc} O^* & (1) & O \\ \parallel & & \parallel \\ ArOCOAr & \rightarrow & [ArO \cdot \cdot COAr] \end{array}$$
(7)

A second possibility follows from process (8), a singlettriplet intersystem crossing, and invokes the hydrogen abstraction reaction (9).

$$E_2(^{l}\pi^* \ge C = 0) \rightarrow E_3(^{3}\pi^* \ge C = 0)$$
(8)

$$E_3 + RH \rightarrow R + ArO\dot{C}(OH)OAr$$
 (9)
XI

Production of aryloxyl radicals from radical species XI would involve formation of an unusual carbene intermediate (9a).

$$XI \rightarrow ArO + HO\ddot{C}OAr$$
 (9a)

Possible reactions of such a carbene intermediate are rearrangement to an aryl formate or insertion reactions with solvent or reactant.

$$\begin{array}{rcl} & O \\ & \parallel \\ HO \ddot{C}OAr & \rightarrow & HCOAr + CH \text{ insertion products (10)} \end{array}$$

Subsequent reactions which are possible are discussed below.

The quantum yields for aryloxyl radical formation from the polymer samples and the p- α -cumyl-substituted model VIIa are substantially lower than those for the ptert-butyl-substituted model I (Table IV). The ϵ_M values for I and VIIa (Table II) indicate an intensity enhancement of about 2 in the 260-nm absorption region when the *tert*-butyl substituent is replaced by the α -cumyl group. This is somewhat larger than is expected if the terminal benzene and diaryl carbonate groups in VIIa were functioning as independent chromophores. To the extent that there is indeed an electronic interaction between these groups as suggested by the spectral data, a radiationless internal conversion process, which competes with the photochemical reactions, is introduced. The net result of such an interaction is to distribute the electronic excitation over an extended π system with increased probability of electronic to vibrational energy conversion and a net reduction in the efficiency of process (3).³⁹

- (38) For a review, see N. J. Turro, J. C. Dalton, and D. S. Weiss in "Organic Photochemistry," O. L. Chapman, Ed., Vol. 2, Marcel Dekker, New York, N. Y., 1969, pp 1-14.
- (39) D. Belluš (private communication) has noted, however, that the quantum yield for the formation of ortho-rearrangement products of

Secondary Stages. Insofar as the homolysis reaction and subsequent processes are concerned, the triplet hydrogen abstraction reaction (9)¹³ provides an explanation which fits the following observations more satisfactorily than the α -cleavage reaction (7).

First, no direct esr^{12,13,40a-c} or optical evidence^{40a,c} for the formation of aryloxycarbonyl radicals has been presented for the diaryl carbonate or polycarbonate systems.

Secondly, it seems unlikely that the proportion of geminate cage recombination of the radicals (no net reaction) produced *via* (7) should be the same in such diverse structures as represented by the acyclic, cyclic, and poly(aryl carbonate ester) samples.

Third, the aryloxycarbonyl radical is quite unstable with respect to decarbonylation and aryloxyl radical formation.^{16,41} Formation of two aryloxyl radicals in the solvent cage undoubtedly would lead to a high proportion of CC coupling products, which cannot be present in these reactions (vide infra).

However, regardless which mechanism holds, in the polymer samples the excited triplet carbonyl or solventderived radicals R· are generated in a region with a high local concentration of methyl groups which are part of the polymer backbone structure. The following mechanism⁴² is proposed to explain the observation that the quantum yield for stable chain breaks exceeds that for scission of the carbonate ester groups, which involves aryloxyl radical formation. (Note: ϕ represents the *p*-phenylene group, $-C_6H_4$ -, in the polymer chain.)



The characteristic absorption of the quinone methide chromophore in XII⁴³ lies in the same wavelength region ($\lambda_{max} < 350$ nm) as the intermediates and final Fries products absorb and would not be distinguishable in these experiments. Tautomerization of XII could yield either a hydroxystilbene chromophore or an α -substituted hydroxystyrene derivative as stable products (XIIIa and b, respectively) under flash photochemical conditions.

The ϕ_d and ϕ_{ArO} values indicate that the total number of chain breaks exceed ester bond cleavages by about 40%.

p-methyl- and p-dodecylphenyl trifluoroacetate in n-hexane (253.7nm irradiation) differ by an order of magnitude (0.11 and 0.015, respectively). Thus an extended π system is not an essential feature for the argument that increasing the internal degrees of freedom as in this case can lead to a reduction in a photochemical process.

- (40) (a) J. A. McRae and M. C. R. Symons, J. Chem. Soc., B, 428 (1968);
 (b) A. R. Lyons, M. C. R. Symons, and J. K. Yandell, J. Chem. Soc., Faraday Trans., 2, 68, 495 (1972); (c) J. S. Humphrey, Jr., and R. S. Roller, to be published.
- (41) Y. Shigemitsu et al., Bull. Chem. Soc. Jap., 39, 2463 (1966).
- (42) For a recent contribution to the literature of 1,2-aryl shifts in radicals and a listing of pertinent references, see P. Cote and B. Vittemberger, J. Amer. Chem. Soc., 93, 276 (1971).
- (43) H. D. Becker, J. Org. Chem., 30, 982 (1965); L. K. Dyall and S. Winstein, J. Amer. Chem. Soc., 94, 2196 (1972).



and if no correction is made for the polar end group effect upon the GPC-derived M_n values, the factor increases from 1.4 to 2.5. However, although these values indicate that reaction (11) would have produced significant quantities of XIIIa and -b, the absorption characteristics⁴⁴ of the two are such that they would not be readily discernible in the final product spectra of the polymer samples (Figure 6).

Carbon-carbon coupling reactions must be considered in systems where aryloxyl radicals are formed. If kinetically free para-substituted aryloxyl radicals yield products like XIVa, -b, or -c (12-14) in the polymer systems, the result is a redistribution of the molecular weight. The accuracy of the GPC-derived M_w/M_n values is not sufficient to ascertain whether this is the case in these reactions, especially since the values for the flashed samples reflect an extreme correction for the polar end groups effects upon M_n . However, if reactions (12-14) occurred to any large extent, then the spectroscopically unobservable chain breaking process would be considerably more efficient than comparison of the ϕ_d and ϕ_{ArO} values would suggest.

The product spectra taken about 1 min after flash photolysis of the acyclic model compounds and polymer samples are strikingly similar (Figure 5). The shoulder absorption at ca. 400 nm is probably due to unreacted aryloxyl radicals. The assignment of the absorption at ca. 385 nm, however, is uncertain. It must represent a product⁴⁵ derived directly from the aryl carbonate chromophore because it arises in spectra of the polymer samples and model compounds; it seems likely that it is due to VIb.⁴⁶

Summary

The quantum yields for the photo-Fries reaction of model compounds I, V, VIIa, and polycarbonate of VIIIa in Cl₂Et solvent are essentially the same: ϕ_{Sal} (av) = 0.18 \pm 0.02. While the quantum yield for aryloxyl radical formation from I is about the same as ϕ_{Sal} , it is considerably



lower for VIIa and polycarbonate, ϕ_{ArO} . VIIa = 0.085. A 1:1 stoichiometry is indicated by the equivalence of ϕ_{ArO} . and ϕ_{ArOH} values for either I, VIIa, or the polymer samples. There was no effect of initial $M_{\rm n}$, $(M_{\rm w}/M_{\rm n})$, or the presence of uncapped phenolic end groups upon the transient absorption spectra of the polymer samples in the 300- to 450-nm region, and the spectra were equivalent to that observed with model compound VIIa. However, the quantum yield for chain breaking, $0.11 \leq \phi_d < 0.22$, is significantly larger than ϕ_{ArO} or ϕ_{ArOH} for the polymer samples; this indicates that a spectroscopically unobservable chain scission occurs as efficiently as scissions of the ester group. These results can be accommodated within the framework of a previously proposed mechanism which specifies that ortho-Fries rearrangement occurs by a concerted, intramolecular route and intermediate free radicals arise from a lower energy excited state which is populated via a conformationally sensitive radiationless energy transfer between the initial phenolate π^* state and the carbonyl group. The extraneous chain-breaking process may be initiated by radical abstraction of hydrogen from methyl groups in the polymer backbone.

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^{(44) (}a) A. E. Lutskii et al., Zh. Obshch. Khim., 35, 2073 (1965); (b) B. J. Finkle et al., J. Biol. Chem., 237, 2926 (1962).

⁽⁴⁵⁾ Although o-diphenoquinones have a characteristic absorption band at ca. 380 nm it is unlikely that the unassigned band in these product spectra is due to XIVb because there is no characteristic blue color when viewed down the length of the 12-cm reaction vessel; D. Schulte-Frohlinde and F. Erhardt, Annalen, 671, 92 (1964).

⁽⁴⁶⁾ The 9-msec transient absorption spectrum of cyclic esters V (Figure 6, ref 1) and the spectral characteristics of 6-acetoxy-2,4,6-trimethyl-cyclohexa-2,4-dien-1-one (G. Quinkert, B. Bronstert, and K. R. Schmieder, Angew. Chem., 84, 638 (1972)) are in accord with this suggestion. Furthermore, the lifetime of VIb is probably many seconds (see footnote 19, ref 26, and ref 27).