ACTH$^{1-10}$ but to a peptide bond at this position in ACTH$^{1-24}$. Comparison of ACTH$^{11-24}$ with the difference spectrum indicates variations between 8.4 and 8.5 ppm. End effects can account for this difference since in ACTH$^{11-24}$ peptide NH resonances near the protonated free N-terminal end are deshielded when compared with the same resonances in ACTH$^{1-24}$ where there is a peptide bond. Thus end effects can account for what apparently look like large differences in the peptide NH region. The Trp-9 indole NH resonance at 10.15 ppm, the Tyr-2 peptide NH proton at 8.75 ppm, and the His-6 C-4 resonance at 7.05 ppm show small chemical shift variations between ACTH$^{1-10}$ and ACTH$^{1-24}$ since they do not exactly cancel out in the difference spectrum. The doublets at 6.75 and 7.25 ppm in the difference spectrum correspond to the aromatic protons of Tyr-23. These resonances were not well resolved in ACTH$^{11-24}$ from the superimposable side chain arginine NH resonances. In summary, the addition and difference spectral studies in the 6.5–9.0-ppm region indicate no interaction between sequences 1–10 and 11–24 in ACTH$^{1-24}$ in acidic solution.

Addition and difference spectral analysis of the peptide CH resonances extending over 3.5–5.0 ppm are outlined in Figures 2–4. Peptide CH resonances in a helix are known to come upfield from their relative positions in a coil in polar nonaqueous solvents. End effects discussed earlier for the peptide NH region apply here also although their magnitude and direction are known with less certainty. There is a sharp side band ~100 Hz upfield from the HOD resonance.

Figure 2 outlines a comparison of the 3.5–5.0-ppm peptide CH region of ACTH$^{1-24}$ with the addition spectrum (ACTH$^{1-10}$ + ACTH$^{11-24}$). The spectra are very similar. The evaluation of end effects in the peptide CH region is not known. Figure 3 outlines the spectrum of ACTH$^{1-10}$ in the peptide CH region along with the difference spectrum (ACTH$^{1-24}$ − ACTH$^{11-24}$). Other than a shift from 4.4 ppm in ACTH$^{11-24}$ to 4.5 ppm in ACTH$^{1-24}$, the spectra lack differences. Comparison of the difference spectrum (ACTH$^{1-24}$ − ACTH$^{1-10}$ with ACTH$^{11-24}$ in the 3.5–5.0-ppm region is outlined in Figure 4. The patterns in the two spectra are similar. The data indicate that the addition and difference spectra in the peptide CH region do not provide evidence for interactions between sequences 1–10 and 11–24.

Mass Spectral Characteristics of Poly(4,4′-isopropylidenediphenyl carbonate)

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ABSTRACT: The mass spectra have been obtained for 4,4′-isopropylidenediphenol (IDP), the diphenyl carbonate of IDP (I), the biscarbonate of IDP (II), the cyclic trimer (III) and tetramer (IV) carbonates of IDP, and poly(4,4′-isopropylidenediphenyl carbonate) (V). Fragments of mass up to *m/e* 762 corresponding to the cyclic trimer have been observed at sample probe inlet temperatures of 250–400°. The spectra show characteristic patterns which correlate with the loss of methyl groups and carbon dioxide and with hydrogen rearrangement reactions which occur during the loss of aryloxy groups from aryl ethers and during the loss of carbon dioxide. These patterns are consistent with those observed for diphenyl carbonate by others and for the model compounds I and II. They are confirmed by metastable patterns and precise mass measurements.

The mass spectral characteristics of poly(4,4′-isopropylidenediphenyl carbonate) (Lexan resin) have been determined and correlated with those of diphenyl carbonate,[1,2] 4,4′-isopropylidenediphenol (IDP), the diphenyl carbonate of IDP, the carbonate of isopropylidenediphenol, and the cyclic trimer and tetramer IDP carbonates. The techniques used have been previously described in reports on the mass spectral characteristics of poly(*p*-xylylene),[3] poly(pivalolactone),[4] and poly(2,6-dimethyl-1,4-phenylene ether).[5] Fragments of mass up to *m/e* 762 have been observed and the degradation patterns correlated with those of related structures.[6–15]

Experimental Section

The poly(4,4′-isopropylidenediphenyl carbonate), the acyclic dimer, and the cyclic trimer[16] and tetramer[16,17] were kindly supplied by Dr. Arnold Factor of the General Electric Co. Research and Development Center. This polymer is terminated with a monofunctional phenol, has a residual hydroxyl content of less than 0.05 wt %, has an intrinsic viscosity of 0.49 dl/g, and is a typical unstabilized commercial (G.E.) polymer. Diphenyl carbonate (DPI-655) was used as received. 4,4′-Isopropylidenediphenol (DPI-6767) was used as received, after careful recrystallization (mp 157°) from benzene, and as the residue left after essentially complete dissolution in hot benzene. The diphenyl carbonate of 4,4′-isopropylidenediphenol (previously undescribed) was prepared by Mr. K. S. Kim using the Schotten–Baumann technique and was recrystallized twice from ethanol, mp 102–103°.

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Anal. Calcd for $C_{29}H_{24}O_6$: C, 74.34; H, 5.16. Found: C, 74.23; H, 5.17.

The mass spectrometer used in these studies was a medium resolution, cycloidal path instrument (Varian M66) with variable slits. The variable temperature inlet probe was calibrated outside the source. The instrument was routinely monitored for background and operated well above the appearance of trace background peaks. The instrument was disassembled and cleaned periodically to remove phenolic residues giving a background peak at *m/e* 213 not removable by ordinary bake-out and evacuation procedures. Resolution was routinely monitored to establish performance at or above the manufacturer's specification of 4000 at minimum slit width. Most observations were made at 1500–2000 resolution for mass ranges below 410. Above 500 the resolution became progressively less. The metastables were observed with wide, but less than maximum slit widths. Precise mass measurements were made at minimum slit width. Additional details of typical operating conditions are given in the legends for Figure 1 which is a reproduction of an actual spectra as recorded. Replicate scans (ten to thirty) were made on several (three to six) samples of each material to establish the reproducibility and reliability of the data. The procedures used in observing spectra changes as the polymer samples were heated to their volatilization temperatures were carefully standardized. Calibrations were made using perfluoroalkane (PFA).

It is to be noted that changes in operating conditions can significantly alter the details of the spectrum. Changes in ion energy and electron voltage produce relatively minor changes. Changes in rate of heating and in analyzer temperature produce marked changes in the relative intensities of larger mass ions and in metastable characteristics. The intensity changes are troublesome in terms of reproducing and recording such data which, for chemical compounds that are stable, are customarily used for characterization. Studies at low analyzer temperatures are difficult because of the background accumulation of contamination for the *m/e* 213 fragment. The relative intensities are usually taken from spectra recorded at wide sweep rates (50 or 100 scale) of necessity in work with M66 spectrometer.

Results

The mass spectrum, as actually recorded, is shown in Figure 1 for polymer (Lexan resin) V. The details of the spectra of other compounds will be summarized in the following paragraphs.

4,4′-Isopropylidenediphenol (IDP). The major peaks in the mass spectrum (70 eV, sample temperature 65°, 4×10^{-7} Torr, analyzer temperature 200°) occur at *m/e* 228, 213, 197, 181, 165, 152, 135, 119, 115, 107, 99, 91, 77, 65, 55, 51, 43, 41, and 39. The relative intensities are as follows for data taken from spectra run at analyzer temperatures of 150° and at wide sweep widths: *m/e* 229 (3), 228 (17), 214 (17), 213 (100), 198 (2.1), 197 (2.3), 195 (0.7), 183 (0.9), 181 (0.6), 169 (1.3), 168 (0.7), 165 (1.7), 152 (1.4), 139 (0.9), 135 (50), 119 (14), 115 (2.3), 107 (4.5), 106.5 (2.6), 99 (7), 95 (14), 94 (1.6), 91 (7.3), 90 (1.9), 89 (1.3), 77 (4), 76 (1.4), 65 (5.4), 63 (2.3), 55 (2.3), 53 (7.2), 51 (2.4), 43 (1.2), 41 (4.3), 39 (5.4). At analyzer temperatures of 200° the relative amounts of *m/e* 228 and 213 are decreased by a factor of 10–15 and the relative amounts of the fragments below *m/e* 135 show some changes. The ratio of 229/228 and 214/213 is 0.165:0.170 in several spectra in accord with the theoretical values for $^{13}C_{15}$. There are half mass peaks at *m/e* 106.5, 105.5, 99.5–96.5, 90.5–87.5, 85.5–81.5, 78.5–75.5, 69.5–70.5, 63.5–65.5, and 57.5. Some of these are notably intense: *m/e* 106.5 (18.3), 99.5 (6), 98.5 (6), 72.5 (4) (per cent relative to 119); others are missing; *i.e.*, no 135/2 = 67.5; 119/2 = 59.5; 107/2 = 53.5. The mass assignments for the major peaks were made with perfluoroalkane as a standard. Precise mass measurements gave values of $C_{13}H_9O$ 181.061 (calcd 181.065), one-half of $C_{13}H_{10}O_2$ 99.027 (calcd 99.034), and C_7H_7 91.052 (calcd 91.055). The only difference noted among unrecrystallized, recrystallized, and residual undissolved samples was a peak of very low intensity at *m/e* 253 not seen in the recrystallized material. This peak also occurs in some of the spectra of the higher mass compositions. The metastable broad peaks are observed centered at *m/e* 250 and 233 (analyzer 200°), 269, 235 (analyzer 150°), 121, 47, 43, 26, 23.5, 22, 19.5, and 13.

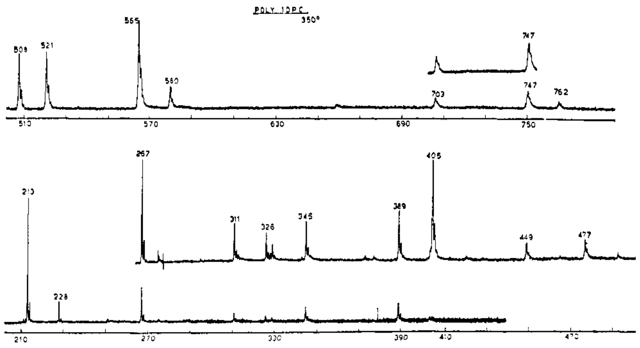

Figure 1. Mass spectrum of poly(4,4′-isopropylidenediphenyl carbonate) (V): electron energy 70 eV, ion energy 76 eV, sample inlet probe 350°, analyzer 150°, pressure 305×10^{-7} Torr, mass ranges 200–500 (lower) and 500–790 (upper) amu.

Isopropylidenediphenyl Bis(phenyl carbonate) (IDP-PC) (I). The main peaks in the spectrum (70 eV, sample temperature 120°, 4×10^{-7} Torr, analyzer temperature 200°) occur at *m/e* 468, 453, 409, 365, 333, 289, 272, 211, 195, 181, 179, 167, 152, 135, 119, 102, 94, 91, 77, 65, 51, 44, and 39. The relative peak heights are given in parentheses and are taken from spectra run at an analyzer temperature of 150°, probe temperature of 190°, and at wide sweep widths: 469 (7.0), 468 (20), 455 (7.6), 454 (31), 453 (100), 424 (0.5?), 410 (6.6), 409 (20), 365 (4.2), 334 (4.0), 333 (13.6), 290 (4), 289 (11.4), 272 (2), 255 (1), 228 (1.0), 214 (5.4), 213 (29), 211 (4.8), 195 (4.0), 135 (4.2), 119 (5.0), 107 (4.2), 94 (5.3), 91 (4.0), and 77 (14.8). The low mass aromatic peak sequence is weak. Metastable broad peaks occur at 93, 473, and 515. The only prominent half-mass peak occurs at *m/e* 106.5. The mass assignments for the major peaks were made with perfluoroalkane as a standard.

Bis(4,4-isopropylidenediphenol) Carbonate (II). The spectra (70 eV, 6–12 $\times 10^{-7}$ Torr, sample temperature 85–230°) for this diaryl carbonate were recorded at analyzer temperatures of 150 and 200°. Mass assignments for the major peaks in the 200-510 range were made using perfluoroalkane as a standard. The spectrum shows peaks at values (*m/e* 508, 703, 747, 762) above that for the molecular ion (*m/e* 482) and these vary in intensity depending on the length of time and the temperatures at which the sample is held in the sample inlet probe. That at *m/e* 508 appears (at 85°) soon after the *m/e* 482 (and *m/e* 467) peaks appear. The low mass spectrum under these conditions is essentially that of the polymer, which will be given in detail in a following paragraph. Polymer-derived peaks also appear at 493, 449, and 318. The relative intensities of the peaks in the 300–500 range, which differ from those of the polymer, are as follows: 508 (5.5), 483 (8.0), 482 (23), 468 (37), 467 (100), 449 (6), 423 (31), 318 (27), 303 (70). These values were taken soon after a sample temperature (150°) adequate for the observation of these peaks had been established and just as the high mass peaks (508) began to appear. Metastable broad peaks centered at *m/e* 233 and 263 are observed. Under reproducible conditions the parent peak at *m/e* 213 is observed in the shape characteristic of a half-life time comparable to the time of flight as described by Beynon.[18] Precise mass determination of the *m/e* 169 peaks gives an observed value of 169.059 (calcd for $C_{12}H_9O$, 169.065).

Cyclic Trimer (III). The mass spectra for the cyclic trimer from IDP were obtained at a sample inlet probe temperature of 190–310°, analyzer temperature of 200°, electron energy of 70 eV, ion energy of 72–74 eV, and pressures of 2–4 $\times$ 10^{-7} Torr. The peak at *m/e* 747 is insensitive to changes in electron energy in the 40–70-eV range. The principal peaks above 230 amu occur at 764 (1.0), 763 (3.6), 762 (5–8), 749 (4–5), 748 (9–12), 747 (13–20), 705 (2), 704 (5–10), 703 (8–13), 660 (2), 659 (3–5), 565 (8), 510 (3), 509 (11), 508 (30), 467 (2–4), 450 (4), 449 (11), 423 (10), 407 (6), 406 (27), 405 (77), 229 (3.6), 228 (18), 215 (3), 214 (17), 213 (100) in the 250–300° spectra. The intensities relative to the to the 213 peak are given in parentheses and are reasonably reproducible in the high mass range for a given sample when equlibrium pressure conditions have been established. There is some change in the relative intensities of the peaks over 400 amu at sample temperatures of 250 and 310° as indicated by the range of values listed. The relative intensities of the peaks over a short mass range can be determined reproducibly and precisely. The intensities of the M + 1 peaks are slightly greater than theory for the carbon-13 isotope content of the high mass peaks. The range is 59–62% (49.5% calcd) for $^{13}C_{45}$, 37.5% (33% calcd) for $^{13}C_{30}$, and 16.3% for $^{13}C_{15}$. The peak pattern below 230 amu is that shown by the polymer with principal peaks at 165, 152, 135, 119, 107 w, 91, 83, 71, 69, 57, 55, 44, 43, 41, 40, and 39 amongst others. The mass numbers were assigned by calibrations with perfluoroalkane at *m/e* 508, 405, 389, 228, and 213. Careful mass measurements on the peaks at 508 and 405 amu were made against perfluoroalkane peaks at 505 and 405 to give values of $C_{32}H_{28}O_6$ 508.16 (calcd 508.19) $C_{29}H_{25}O_2$ 405.176 (calcd 405.1848). The residual sample on removal from the analyzer shows no sign of decomposition.

Cyclic Tetramer (IV). The mass spectra for the cyclic tetramer were obtained at sample inlet probe temperatures 230–310°, analyzer temperatures 100–200°, electron energy 70 eV, ion energies 74–78 eV, and pressures 0.8–10 $\times$ 10^{-7} Torr. The principal peaks above 210 amu occur at *m/e* 762 (36), 747 (103), 703 (60), 508 (163), 449 (68), 405 (420), 228 (16), 213 (100). The intensity data are from a spectrum run at 310° sample probe temperature. These peaks are associated with M + 1 and M + 2 peaks of slightly greater than theoretical isotopic intensity. Peaks of less (10–35) intensity occur at *m/e* 660, 659, 565, 521, 493, 467, 389, 377, 345, 329, 322, 313, 297, 267, 251, and 228. The low mass spectrum resembles that of the polymer with major peaks at *m/e* 197, 194, 181, 179, 178, 165, 152, 134, 135, 119, 107, 94, 91, 77, 65, 55, 51, 44, 41, 39, and 28. The intensities relative to the 213 peak are given in parentheses and are reasonably reproducible after a sample probe temperature of about 300° is established. At lower sample probe and analyzer temperatures the relative intensities vary. Repeated scanning of the spectrum in the range from 700 to 1030 amu disclosed no evidence of peaks above 765 amu.[18] Changes in analyzer temperature or source temperature did not alter this. There is also no evidence for a peak at 500.5 (doubly ionized 1001 (1016–1015) which should be the most intense peak in this range). It is noted that the intensity of this peak may be below the sensitivity level of the instrument. Mass numbers were assigned by calibration with perfluoroalkane on the *m/e* 213, 228, 405, 508, 705, 747, and 762 peaks and by counts on wide sweep spectra. Data for the precise mass measurements for the peaks at 119 (C_8H_7O), 135 ($C_9H_{11}O$), and 151–153 ($C_{12}H_7$–$C_{12}H_9$) are given in Table I. The peak at 703 amu is not intense enough to permit good resolution but attempts to assign a precise mass gives a value of 703.23 (calcd for $C_{46}H_{39}O_7$ 703.27, and for $C_{45}H_{35}O_8$ 703.23). The former is tentatively considered more nearly correct since a low observed value is characteristic of the instrument settings during these scans.

Table I
Fragment Composition Assignments

Source compd	Fragment composn	Fragment mass Calcd	Fragment mass Obsd	Ref fragment
Polymer	C_2H_4	28.0312	28.0311	N_2
Polymer	CO	27.9949	27.9961	N_2
Polymer	CHO	29.0027	29.0040	C_2H_5
Polymer	C_3HO	53.0027	53.0050	C_4H_5
IDP	C_7H_7	91.055	91.052	CBr
IDP	$(C_{13}H_{10}O_2)_{0.5}$	99.034	99.027	C_2F_4
Polymer	C_7H_7O	107.0495	107.0495	C_2H_4Br
IV	C_8H_7O	119.060	119.050	C_2H_5
IV	$C_9H_{11}O$	135.0807	135.0804	C_2F_4Cl
IV	$C_{12}H_7$	151.0547	151.0483	$C_2F_3Cl_2$
IV	$C_{12}H_8$	152.0626	152.0646	$C_2F_3Cl_2$
IV	$C_{12}H_9$	153.0704	153.0662	$C_2F_3Cl_2$
II	$C_{12}H_9O$	169.065	169.059	C_3H_7
IDP	$C_{13}H_9O$	181.065	181.061	C_4H_7
Polymer	$C_{14}H_{13}O_2$	213.0912	213.0917	$C_{13}F_3$
III	$C_{29}H_{25}O_2$	405.1848	405.176	$C_{10}F_{15}$
Polymer	$C_{25}H_{26}O_2$	405.1848	405.179	$C_{10}F_{15}$
III	$C_{32}H_{28}O_6$	508.19	508.16	$C_{12}F_{12}$
Polymer	$C_{39}H_{33}O_4$	565.2370	565.2296	$C_{17}F_{15}$

Poly(4,4′-isopropylidenediphenyl carbonate) (V). The mass spectra (Figure 1) for the polymer were obtained at sample inlet probe temperatures of 220–410°. As the sample is heated to these temperatures, the peaks at *m/e* 213 and 267 appear at 110°. Not below 350° are appreciable amounts of higher mass peaks observed. At 350° peaks in the *m/e* 405–762 range are prominent but their relative intensity varies and it is difficult to obtain the equilibrium needed for precise data over the wide mass ranges involved. The relative intensities of the peaks over a narrow range are fairly reproducible. The intensities of the M + 1 and M + 2 peaks are in excess of those required for the theoretical isotope ratios, *e.g.*, at 508/509 36% (33% calcd) for $^{13}C_{30}$ and at 747/748 61% (49.5% calcd) for $^{13}C_{45}$. Analyzer temperatures of 150–200°, electron energy of 70 eV, ion energies of 82–76 eV, and pressures of 2–10 $\times$ 10^{-7} Torr were used. The principal peaks above 213, with intensities (from 400° spectra) relative to the *m/e* 213 peak in parentheses, are *m/e* 762 (1), 747 (4), 729 (2), 718 (1), 703 (5), 659 (1), 580 (1), 565 (1), 521 (1), 508 (15), 493 (6), 477 (16 , 449 (18), 423 (6), 405 (25), 357 (5), 329 (10), 315 (6), 313 (5), 311 (5), 267 (8), 228 (85), 213 (570). The 762, 747, 703, 508, 405, and 213 peaks are accompanied by peaks at M + 1 and M + 2 with the intensities stated above. Some of the peaks appear at low inlet temperatures but disappear at higher temperatures, *e.g.*, 565, 521, and 267. One (467) appears only at high temperature. Although there are differences in the spectra of the polymer and those of the trimer and tetramer, there has been no observation of a peak of mass over *m/e* 762 nor of half-mass peaks above *m/e* 106.5.[18] Mass numbers were assigned by calibration against perfluoroalkane

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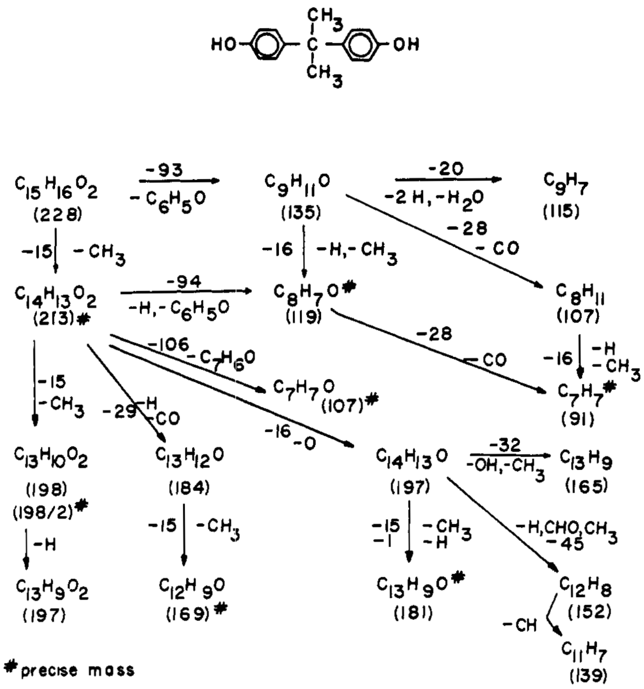
(18) The presence of peaks at approximately *m/e* 1016 and 1001 and fragmentation peaks at *m/e* 957 (−44), 913 (−44), 834 (−79), 819 (−15), 775 (−44), and 762 (−13) have been observed and calibrated against PFA since this writing with both the tetramer and the polymer using an acid stabilization technique. With the polymer there are additional series of peaks separated by intervals of *m/e* 45 and 81 at 913, 858, 843, 799, 754, 729, 685, 604, 589, 545, and 467 suggesting that different fragments, possibly of higher molecular weight, are volatilized from the polymer.

over the mass ranges from *m/e* 213 to 590 and from 700 to 780. The peak at *m/e* 28 is resolved into a triplet (nitrogen, carbon monoxide, ethene), that at *m/e* 29 into a doublet (CHO and C_2H_5), and that at *m/e* 53 into a doublet (C_4H_5 and C_2HO). Precise mass assignments for the peaks at 107.0495 (C_7H_7O), 213.0917 ($C_{14}H_{13}O_2$), 405.176 ($C_{29}H_{25}O_2$), and 565.2296 ($C_{39}H_{33}O_4$) are given in Table I. Metastable broad peaks were observed centered at about *m/e* 335, 270, 235, 220, and 120 and at low mass (*m/e* 39.3, 40.3). The sample is carbonized on removal from the analyzer if heated over about 400°, not if not heated over about 300°.

Discussion

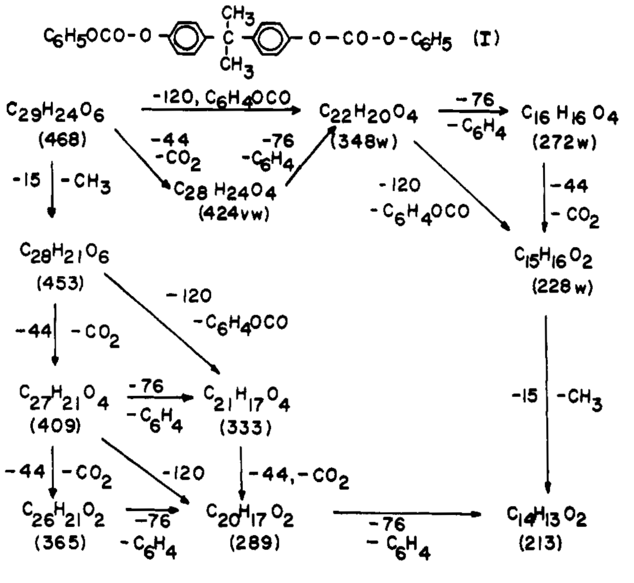
The degradation pattern, summarized in Chart I, for isopropylidenediphenol is rather involved but can be accounted for, at least in terms of most of its major degradation products, by analogy to known transformations of cresols[6-10] and hydroxybiphenyls.[11,12] The initial degradation of the molecular ion involves loss of methyl (228 → 213) or of hydroxyphenyl (228 → 135). The former is clearly supported by the metastable broad peak at 235. The higher metastable peak at 270 is assignable to the loss of hydroxyphenyl from 228 but, since under other conditions this metastable appears as low as 250, it may also be assigned to the loss of C_6H_6O from 213 to give 119. Both may occur. The loss of 28 or 29 (CO or CHO) from the molecular ion is not significant. The demethylated intermediate (213) gives rise to most of the remaining major peaks by loss of methyl (213 → 198), loss of hydroxyphenyl (213 → 119), loss of oxygen or water (213 → 197, 195), and loss of CHO (213 → 184). The doubly demethylated intermediate (198) shows up as its doubly charged ion (99) and loses CHO (198 → 169), OH (198 → 181), or C_6H_3O (198 → 91) to give C_7H_7O (107). The mass 181 intermediate loses CHO (181 → 152) which in turn loses CH (152 → 139). These transformations do not provide a plausible explanation for the peaks at *m/e* 95 and 94. It is to be noted that loss of oxygen as such rather than as hydroxyl or water (*i.e.*, 181 is $C_{13}H_9O$ – precise mass) seems to be involved in some fragmentations and that migration of a methyl or hydrogen to one ring is required in the formation of the *m/e* 107 fragment. The metastable at 120 suggests a loss of 28 from 107 giving 79. The metastables in the range below 50 are probably associated with loss of methine or hydrogen. Precise mass measurements, for which data are given in Table I, confirm the composition of fragments of mass 99 as $C_{6.5}H_5O$ and 181 as $C_{13}H_9O$. The 119 fragment, as derived from the tetramer, is confirmed as C_8H_7O. The *m/e* 107 fragment, as derived from the polymer, is confirmed by precise mass measurement as C_7H_7O and not C_8H_{11} establishing that, for the polymer, and probably also for IDP itself, carbon monoxide is lost from the 119, not the 135, *m/e* fragment. The 135 and 151 fragments from the tetramer confirm the structures $C_9H_{11}O$ and $C_{12}H_7$.

CHART I
FRAGMENTATION PATTERN FOR
4,4′-ISOPROPYLIDENEDIPHENOL



The degradation pattern, summarized in Chart II, for the bis(phenyl carbonate) of isopropylidenediphenol (I) is of value as a reference. The terminal groups in the polymer, as prepared from diphenyl carbonate and the diphenol, are similarly structured. The principal peaks in the spectrum correspond to masses which are in accord with those present in the spectrum of the diphenol, as described above, and of diphenyl carbonate.[1,2,19] The molecular ion (*m/e* 468) undergoes loss of 15 amu (methyl) to give a fragment of mass 453, the most intense peak observed. There is a metastable broad peak centered at *m/e* 473 which may correspond to this loss of 15 amu or to the loss of 44 from 453 to 409. The metastable transition involving loss of carbon dioxide from diphenyl carbonate has been noted before.[2] The further degradation indicates the loss of 76 from 409 to 333 followed by the loss of the second 44 to 289 in turn losing 76 to 213. The 228 mass fragment, the molecular ion of the diphenol, is presumably formed in a hydrogen transfer reaction during decarboxylation or during cleavage of the diaryl ether structure. This fragmentation, leading to fragments of mass 228 and 213, is common to all of the compounds in this series. The processes are outlined in formulas for the polymer. Most of the fragments of lower mass (135, 119, 107, 94, 91, 77, 65, 55, 43) are those ob-

CHART II
FRAGMENTATION PATTERN FOR
4,4′-ISOPROPYLIDENEDIPHENOL
BIS(PHENYL CARBONATE) (I)



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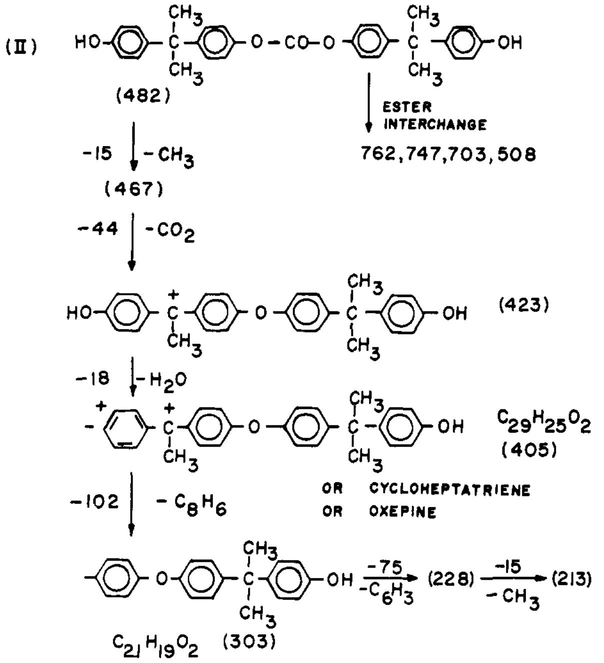
(19) A. Davis and J. H. Golden, *J. Macromol. Sci. Rev. Macromol. Chem.*, 3, 49 (1969).

served with the diphenol itself. Exceptions are the increased amounts of 77, 44, 32, and 28 presumably arising from phenyl, carbon dioxide, oxygen, and carbon monoxide available from the benzoyloxy and carbonate groups. The pronounced metastable broad band at 90–95 is probably asssociated with the loss of 26 from 77 to give 51 amu.

The bis(IDP) carbonate (II) spectra show peaks for the molecular ion (*m*/*e* 482), the molecular ion less 15 (*m*/*e* 467), and the molecular ion less 59 (44 + 15) (*m*/*e* 423). These transformations, summarized in Chart III, correspond to the loss of a methyl and a carbon dioxide fragment. The further loss of water (18) to *m*/*e* 405 is also characteristic of the isopropylphenol structure formed on rearrangement of the carbonate to the di(hydroxyaryl) ether and is consistent with other similar observations.[1,2] The fragment of mass 303 is apparently formed by loss of the aromatic ring (C_8H_6, 102 amu) remaining after the loss of water. The metastable pattern for the conversion of the 213 fragment to 119 by loss of 94 amu appears in the form characteristic of that for an ion losing half its mass in a half-life time comparable to the time of flight. Although noted[13] as a possibility it is not clear whether such a metastable transition has been observed previously.

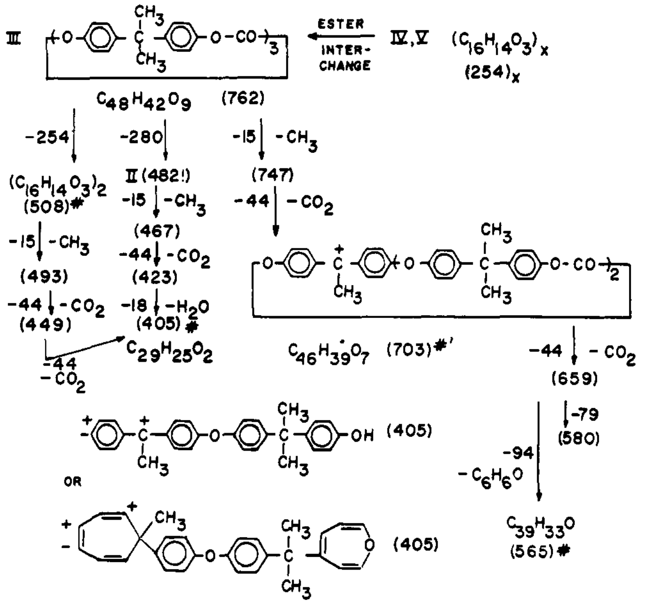
CHART III
FRAGMENTATION PATTERN FOR
BIS(4,4′-ISOPROPYLIDENEDIPHENOL) CARBONATE (II)



The possibility of obtaining reproducible spectra for the carbonate (II) is complicated by the fact that it undergoes ester interchange at the sample inlet probe temperatures required for volatilization. This is apparent in the appearance of peaks corresponding to mass higher than that of the molecular ion almost as soon as the spectrum is recordable. The phenomenon also complicates the interpretation of the spectra for mass numbers below that of the molecular ion by the introduction of peaks derived from the higher mass fragments which in some cases do and others do not coincide with peaks from the diaryl carbonate. The 508 amu mass peak associated with the appearance of the first traces of interchange product is attributable to formation of a cyclic dicarbonate dimer, although such a dimer has never been isolated.

The data from the spectra for the cyclic trimer (III) show the molecular ion at 762 amu and the typical degradation pattern, summarized in Chart IV, involving loss of methyl (762 → 747) and carbon dioxide (747 → 703). Also observed are cleavage (or interchange) to the dimer fragment (762 → 508), to the demethylated dimer fragment (467), and to the dehydrated fragment (405). The last (405) is the most prominent peak above 400 amu and presumably undergoes ring degradation with loss of O or H_2O to give the 228 and 213 peaks as was observed with the dimer (II). There is a question as to whether or not the sample is undergoing ester interchange at the temperature required for volatilization. This is indicated by some changes in the relative intensities of the fragments at 250 and 300°. It is, however, apparently less significant than with the dimer (II), for which such changes are more pronounced, and the polymer for which higher temperatures are required for the sample volatilization. Since the *m*/*e* 762 fragment is the highest mass fragment observed in the spectra from the tetramer and polymer, it seems likely that this is the unit volatilized from such higher molecular weight materials and that it is formed from them by ester interchange.

CHART IV
FRAGMENTATION PATTERN FOR CYCLIC TRIMER III,
CYCLIC TETRAMER IV, AND POLYMER V



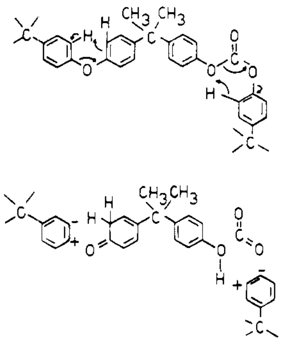
precise mass

The spectra for the tetramer (IV) do not show the molecular ion (1016 amu) or any simple product derived from it by the loss of methyl (1001) or carbon dioxide (972).[18] There is an intense peak at 508 which might be assigned to the doubly charged ion except for the absence of a peak at *m*/*e* 500.5 derivable from the demethylated tetramer ion. It is concluded that under the conditions available in the mass spectrometer used for these studies the temperatures required to volatilize the sample initiate ester interchange to the trimer (762 amu), the highest mass peak seen. Below mass 762 the spectrum resembles that for the trimer except for variations in peak intensities resulting presumably from difficulties in equilibrating the interchange reaction. The increased, as compared to the spectra for the trimer, intensities of the 762, 747, 703, 508, and 405 peaks probably also result from the required use of the higher sample volatilization temperatures. There is nothing significant in the spectra to indicate a different structure or degradation pattern from that outlined in Chart IV.

The spectra for the polymer (Figure 1) show the same general characteristics as do the spectra of the trimer and tetramer. There is no evidence for any fragment of mass over 762.[18] It is necessary to use a somewhat higher inlet probe temperature

(350–410°) than is required for the trimer and tetramer to obtain reasonably intense high mass peaks. Presumably this facilitates ester interchange so that the same products are seen from both the polymer and the oligomers, but it also leads to sample carbonization and presumably to differences in the relative intensities of the low mass peaks. There are enhanced amounts, relative to the *m/e* 213 peak, of the peaks at 197, 135, 121, 107, 94, 91, 77, 65, 51, 39, 28, and 27. The isotope ratios and metastable patterns are similar to those observed with the oligomers. The fragmentation pattern is outlined in Chart IV.

The presence of the intense *m/e* 213 and the *m/e* 228 peak in the spectra of the model compounds and polymers requires comment. These are peaks associated with the molecular ion of the diphenol and are, by analogy with other phenols, assigned hydroxyl or quinoid structures. The source of the hydrogen required for these structures as formed from the esters, oligomers, and polymer is not obvious. The most likely sources are reaction with adsorbed water, an ion–molecule reaction, or a rearrangement. The first possibility has been established for phenols by deuterium oxide equilibration of the inlet.[14,15] The second should be evidenced by changes in relative amounts of 213 and 228 with changes in pressure and repeller voltage. There are some indications of such effects in the present studies, but they have not been examined in detail. The rearrangement reaction involving transfer of a hydrogen is possible during cleavage of the diaryl ether (formed on decarboxylation) or during decarboxylation as indicated.



It is now possible to establish correlations between the fragmentation processes observed with the polymer under electron impact in mass spectrometry and other types of degradation. Thermal and radiative degradations have been well characterized.[19] Thermal degradation under vacuum occurs at or above 360° to give products—carbon dioxide, IDP, carbon monoxide, methane, phenol, diphenyl carbonate, 2-(4-hydroxyphenyl)-2-phenylpropane, ethylphenol, isopropenylphenol, isopropylphenol, and cresol. Most of these are directly related to prominent fragments ($C_9H_{11}O$, C_8H_7O, C_7H_7O) seen in the mass spectra. The dehydroxylated diphenol, however, does not appear in the mass spectra, and dehydroxylation occurs in smaller fragments only as a minor process. Also, the demethylation process, which is most prominent in the mass spectra, does not occur, or gives no isolatable product, in thermal degradation. There appears to be no evidence for the rearrangement to diaryl ether structures in the thermal studies of the polymer itself although the thermal rearrangement of diphenyl carbonate to phenoxybenzoic acid and diphenyl ether are known.[19] The appearance of aryl ether fragments in the mass spectra confirms the possibility, suggested previously,[19] that the polyethers are intermediates in the formation of the diphenol from the polymer.

The high energy (γ rays, electrons) degradation of the polymer gives hydrogen, carbon monoxide, carbon dioxide, and methane.[19] Transformations leading to these products are well defined in the mass spectral data. However, the high CO to CO_2 ratio observed in the radiation processes is not reflected in the mass spectra data, in which it is loss of carbon dioxide that is the characteristically predominant transformation of the carbonate linkage. This is not apparent from the gas analyses and is important in establishing that the excess CO is probably formed from CO_2 and not by direct cleavage of the polymer linkage. Data for diphenyl carbonate confirm these observations. The mass spectra show very little direct evidence for the loss of CO. The most prominent fragmentation peak is that at *m/e* -59 (-15, -44). Thus, it is *m/e* 409 that is prominent from I; 423 from II; 405 from III and IV; and 703 from V. The CO is apparently formed from the phenoxy oxygen after initial cleavage with loss of CO_2. The mass spectral data also favor the cyclic transition state rearrangement, shown in the diagram, over the radical cleavage and recombination alternative. This is consistent with the improbability of molecular collisions in the high-vacuum conditions prevailing in the spectrometer.

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