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On the photolysis of phthalic acid dimethyl and diethyl ester: a product analysis study

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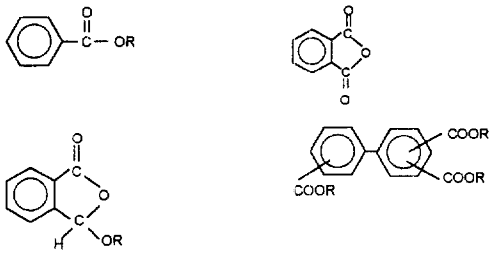
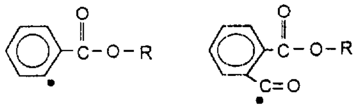
Abstract

Dimethyl phthalate, DMP, and diethyl phthalate, DEP, are rather photostable (Φ(-phthalate) ≤ 0.03). Exposure of neat DMP and DEP in the presence of air to high absorbed doses of UV light yielded a variety of products, many of them identifiable by GC-MS analysis. The products were divided into two fractions by ether extraction. Typical products contained in the ether-soluble fraction of irradiated DMP and DEP are:



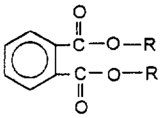
The ether-insoluble fraction consists of oligomeric compounds (molar mass: several 10^3 g mol^{-1}) that are characterized by a high degree of substitution at the aromatic rings and by the existence of conjugated double bonds that act as chromophoric groups absorbing light in the visible wavelength range. Reaction pathways based on the primary cleavage of bonds next to the carbonyl groups and leading to the following radicals are proposed:



Keywords: Dialkyl phthalates; Photolysis; Photoproducts

1. Introduction

Phthalic acid dialkyl esters (1,2-benzene dicarboxylic acid dialkyl esters) of the general structure



(R: alkyl group) are frequently used as plasticizers for polyvinylchloride, PVC. They are quite photoresistant: quantum yields of decomposition Φ(-phthalate) ≤ 0.03 were determined in our former work [1]. However, in long-term outdoor applications, phthalate-plasticized PVC suffers from photodegradation [2–5] and one of the aims of our studies was to find out how the photolysis of the plasticizer contributes to the photodegradation of plasticized PVC. For this purpose, experiments were performed with both neat phthalates [1,6] and phthalate-plasticized PVC [7,8]. The major products generated in the photolysis of neat phthalates with alkyl groups containing many carbons, such as C_8H_{17}, are 1-alkenes, alkyl alcohols, phthalic acid anhydride, 2-formyl

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benzoic acid esters and benzoic acid esters [1,6] indicating that the photolysis of these phthalates originates essentially from reactions involving the carbonyl groups. From a critical analysis of the results, it was concluded that the photodecomposition of the ester groups involves two processes: (i) the simultaneous scission of the two ester groups, leaving the dicarbonic acid structure intact, and (ii) the cleavage of the C–C bond connecting a carbonyl group with the aromatic ring. In the former product analysis study [1] not all photoproducts were identified. For instance, the origin of the quite significant increase in the optical absorption in the wavelength range between 300 and 400 nm was not revealed, and the question whether, apart from the proposed mechanism, also other processes play a role in the photolysis of phthalates remained unanswered. In the present work, it was, therefore, attempted to identify the colored substance(s) and additional products that are generated in minor yields. This task affords, of course, rather high absorbed doses and brings up the problem of discriminating primary from secondary photoproducts. Although the latter problem could not yet be solved satisfactorily, it appears interesting to present new results obtained recently because, in the practical case, a phthalate acting as plasticizer in a polymer matrix is exposed to light over long periods and primary photoproducts are involved in the photoprocesses occurring in the polymer matrix to an extent that increases as the exposure continues. The results reported below pertain to phthalates with small alkyl groups: dimethyl phthalate, DMP, and diethyl phthalate, DEP. These compounds were selected for the sake of simplification, i.e., to avoid complications based on the formation of additional products arising from the decomposition and/or from reactions of long alkyl groups. Actually, DMP and DEP also undergo a pronounced discoloration upon exposure to UV light.

2. Experimental details

2.1. Materials

Dimethyl phthalate, DMP and diethyl phthalate, DEP, obtained from E. Merck were subjected to vacuum distillation prior to use.

2.2. Irradiations

The phthalates were exposed to UV light under air at 35°C between two quartz plates (75 × 15 × 0.5 mm, optical path length: 0.5 mm, t_{irr}: up to 30 h). The light source was that of a Minicure apparatus (Primac, Jiggs and Lamps, UK). This apparatus contains a medium pressure mercury lamp emitting several lines between 240 and 440 nm. No filter was used. Although the exposures were performed under air, it appears that O_2 should have affected the photolysis only weakly. This follows from the fact that only a small portion (c. 4%) of the sample area was exposed to air during the irradiation. Consequently, all O_2 contained initially in the sample must have been consumed quickly in the initial stage of the irradiation. Later, the photolysis in the bulk of the substance proceeded practically in the absence of O_2.

2.3. Treatment of irradiated samples

The irradiated samples, being of yellowish color, contained products of varying molar mass. For the analysis of the high molar mass fraction, the irradiated sample was extracted with diethyl ether, which readily dissolved the low molar mass fraction. The ether-insoluble fraction was dissolved in methanol (in the case of DMP) or in acetone (in the case of DEP) and precipitated with diethyl ether. After this procedure was repeated five times, the residual material was dissolved in toluene (in the case of DEP) or in toluene containing 5% methanol (in the case of DMP). These solutions were applied to a chromatographic silica gel column (i.d. = 3 cm; filling material: 40 g Kieselgel 40, E. Merck, 70–230 mesh, ASTM). Notably, the injected material was not eluted from the column when toluene served as eluant. However, it was extracted from the column when methanol/toluene mixtures were employed as eluants. Actually, several different fractions were extracted by varying the methanol/toluene volume ratio over a wide range from 5:95 to 80:20. The fractions were subjected to IR and NMR analysis after evaporation of the solvent.

For the analysis of the low molar mass fraction, the irradiated sample was washed briefly with a small amount of methanol. Thereby, the high molar mass fraction remained undissolved and the low molar mass fraction including the non-reacted phthalate was extracted. The colorless methanol solution obtained in this way was freed from solvent and subjected to gas chromatographic analysis.

2.4. Characterization of photoproducts

2.4.1. Gas chromatography

A Varian 3700 gas chromatograph equipped with a quartz capillary column (Permaphase PVMS/54); length, 25 m; i.d. = 0.3 mm) was used. It was operated in conjunction with either a flame ionization detector or with a mass spectrometer (Varian MAT 44) employing the electron impact (EI) method. After injection of the sample (injector temperature: 290°C), the oven temperature was kept constant for 5 min at 40°C. Subsequently, it was increased at a rate of 10°C/min to 290°C and kept at this level for 15 min. Notably, identical chromatograms were recorded with both detectors.

2.4.2. Liquid chromatography

The ether-insoluble fraction was subjected to size exclusion chromatography performed with four Styragel columns (porosity: 10^5, 10^4, 10^3 and 5×10^2 Å) in conjunction with a RI detector. Tetrahydrofuran served as eluant.

2.4.3. IR spectroscopy

A Bio-Rad spectrometer, model FTS-7IR, was used. The spectra were recorded with KBr pellets.

2.4.4. NMR spectroscopy

^{1}H NMR spectra were recorded with instruments from Bruker (200 MHz) or Varian (EM 390, 90 MHz). Perdeuterated solvents were used (methanol or acetonitrile/tetrahydrofuran mixture).

3. Results

Upon exposure to UV light, the phthalates attained a yellowish color. When the irradiated material was extracted with diethyl ether, two fractions were obtained: a transparent ether-soluble one and a colored ether-insoluble one. Both fractions were soluble in methanol, but the low molar mass fraction dissolved much faster than the high molar mass fraction. Based on this fact, fractionation by selective extraction with methanol was performed when the GC-MS technique was employed for the analysis of the low molar mass fraction. The analysis of the two fractions is described below.

3.1. Analysis of the low molar mass fraction

Gas chromatograms of the unirradiated phthalates and of the low molar mass fractions of irradiated DMP and DEP recorded with the aid of the MS detector are shown in Fig. 1. The unirradiated phthalates (a-1 and b-1) contain small amounts of impurities. DMP contains diethyl phthalate eluting at $t_{\mathrm{ret}} = 20.05$ min, and DEP contains dimethyl phthalate, ethyl butyl phthalate, dibutyl phthalate and dipentyl phthalate eluting at $t_{\mathrm{ret}} = 18.06$, 22.06, 24.99 and 27.00 min, respectively. The low molar mass fractions of DMP and DEP irradiated for 16 h contain a broad spectrum of compounds as can be seen from the chromatograms, a-2 and b-2 in Fig. 1. Lists of the peaks with the corresponding retention times are presented in Tables 1 and 2. These tables also contain peak assignments made on the basis of both the highest m/e value of the mass spectrum and of the ion decomposition pattern constructed for best fit with the mass spectrum. For the sake of brevity, only a few typical mass spectra namely, those of the products M-1, M-5, M-15 and M-17, generated in the photolysis of DMP, are presented in Fig. 2. The corresponding ion decomposition patterns and, in addition, that concerning M-13/M-14 are shown in Scheme 1. It is interesting to note that the 3-alkoxyphthalides M-5 and E-4 are formed as major products in the photolysis of DMP and DEP, respectively. Notably, the mass spectrum of E-4 is identical with that of 3-ethoxyphthalide reported by Spangler et al. [9]. Other major products are: phthalic acid anhydride (M-3, E-2), the terephthalic acid esters M-6 and E-5, the m-phthalic acid ester M-7 and the semi esters M-10 and E-6. In the latter cases, the MS-GC analysis clearly excluded an assignment to the semi esters of o-phthalic acid.

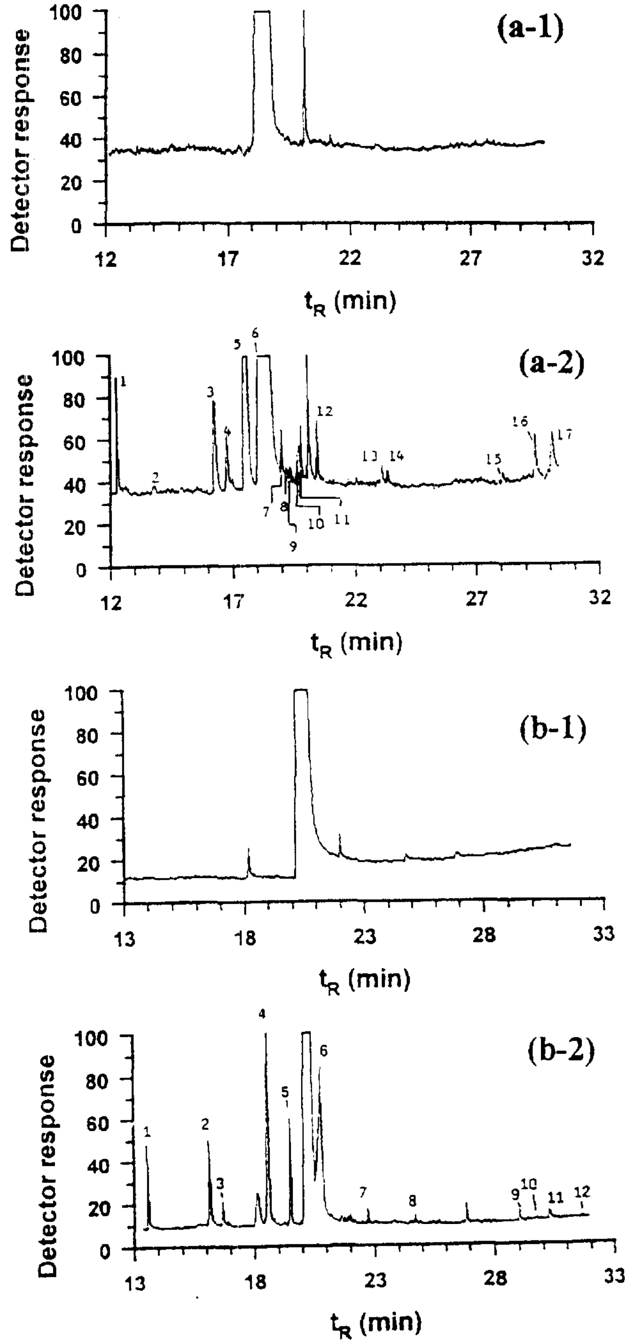


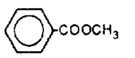
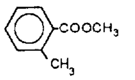
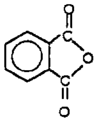
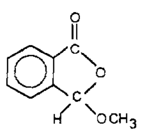
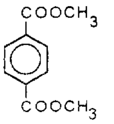
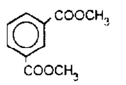
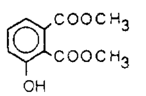
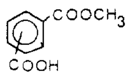
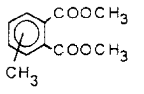
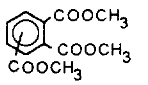
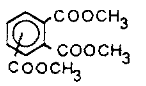
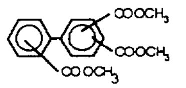
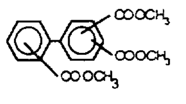
Fig. 1. Gas chromatograms of unirradiated DMP (a-1) and DEP (b-1) and of the low molar mass fractions of irradiated DMP (a-2) and DEP (b-2). The phthalates were irradiated for 16 h between quartz plates.

3.2. Analysis of the high molar mass fraction

3.2.1. Size exclusion chromatography

As can be seen from Fig. 3, the SE chromatogram of the ether-insoluble fraction obtained from irradiated DMP exhibits a peak at $V_{\mathrm{E}} \approx 39$–40 ml, i.e., at an elution volume definitely lower than that of the unirradiated neat phthalate (at about $V_{\mathrm{E}} = 43$ ml). It is, therefore, concluded that the ether-insoluble fraction consists of compounds of relatively

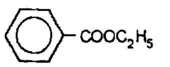
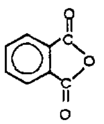
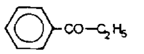
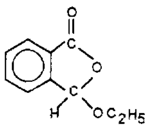
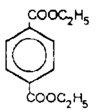
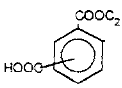
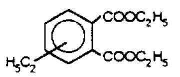
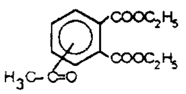
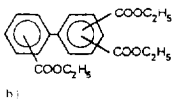
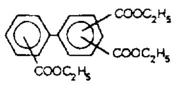
Table 1
Products of the photolysis of DMP

Peak number	Retention time (min)	Compound	$m_{calc} = m_{ms}$ [a]
M-1	12.18		136
M-2	13.84		150
M-3	16.06		148
M-4	16.42	b)	134
M-5	17.30		164
M-6	17.54		194
M-7	19.00		194
M-8	19.12	b)	208
M-9	19.18		210
M-10	19.42		180
M-11	19.48		208
M-12	20.30	b)	
M-13	23.06		252
M-14	23.18		252
M-15	28.00		328
M-16	29.18	b)	
M-17	30.00		328

[a] m_{calc}: calculated mass of parent ion; m_{ms}: mass corresponding to ion of highest detectable mass.
[b] unidentified.

high molar mass. Quite analogous results were obtained in the case of DEP (not shown here).

Table 2
Products of the photolysis of DEP

Peak number	Retention time (min)	Compound	$m_{calc} = m_{ms}$ [a]
E-1	13.36		150
E-2	16.06		148
E-3	16.42		134
E-4	18.36		178
E-5	19.30		222
E-6	20.54		194
E-7	22.42		250
E-8	24.36		264
E-9	29.06	b)	
E-10	29.48		370
E-11	30.18	b)	
E-12	31.42		370

[a] m_{calc}: calculated mass of parent ion; m_{ms}: mass corresponding to ion of highest detectable mass.
[b] unidentified.

3.2.2. UV absorption spectra

Fig. 4 presents UV/VIS absorption spectra of the unirradiated neat phthalates and of subfractions of the ether-insoluble portions. Contrary to the spectra of the neat phthalates, the spectra of the subfractions are structureless and extend to wavelengths up to about 550 nm.

3.2.3. ^1H NMR spectra

Figs. 5 and 6 present ^1H NMR spectra of the ether-insoluble fractions of irradiated DMP and DEP, respectively, and for the sake of comparison also the spectra of the unirradiated phthalates. Three different kinds of protons can be discriminated in the case of unirradiated DMP: methyl protons (H^a) and two kinds of *aromatic* protons (H^b and H^c). The spectrum of the photoproduct contains a new band at 3.6 ppm that is

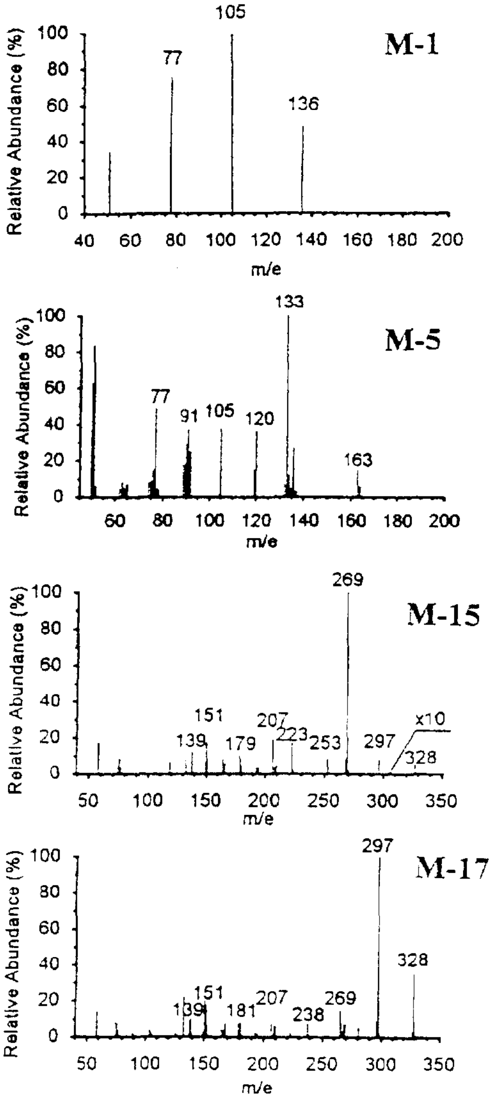


Fig. 2. Mass spectra of products M-1, M-5, M-15 and M-17 generated in the photolysis of DMP.

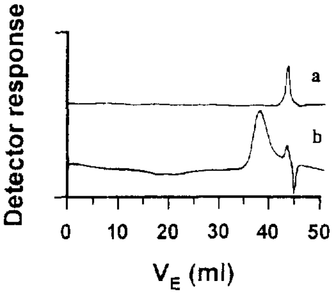


Fig. 3. Size exclusion chromatograms recorded with unirradiated DMP (a) and with the high molar mass fraction generated in the photolysis of DMP (b). Eluent: THF.

assigned to methyl protons (H^a) of ester groups attached to C=C double bonds [10]. A likely structure is shown in Fig. 5. Moreover, the band of the (aromatic) H^b protons is larger than that of the (aromatic) H^c protons indicating that a significant portion of H^c protons has been substituted by other groups. A high degree of substitution in the photoproduct is also inferred from the fact that the ratio of aromatic to aliphatic protons is lower in the irradiated material than in pristine DMP. Similar conclusions can be drawn by inspecting the spectra recorded with unirradiated DEP and the corresponding photoproduct (see Fig. 6). In the case of the unirradiated DEP, four different kinds of protons can be discriminated: methyl protons (H^a), methylene protons (H^b) and two kinds of *aromatic* protons (H^c and H^d). The spectrum of the photoproduct contains new bands at 1.2 ppm (H^a), 4.3 ppm (H^b) and between 3.4 and 3.9 ppm (H^c). Regarding H^a and H^b assignments to methyl and methylene protons, respectively, located in ester groups attached to carbon–carbon double bonds appear likely (see formula shown in Fig. 6). Moreover, as in the case of DMP, the band of the (aromatic) H^c protons is larger than that of the (aromatic) H^d protons. Finally, the bands between 3.4 and 3.9 ppm are attributed to hydrogens of type H^c located at tertiary carbons (vide formula shown in Fig. 6).

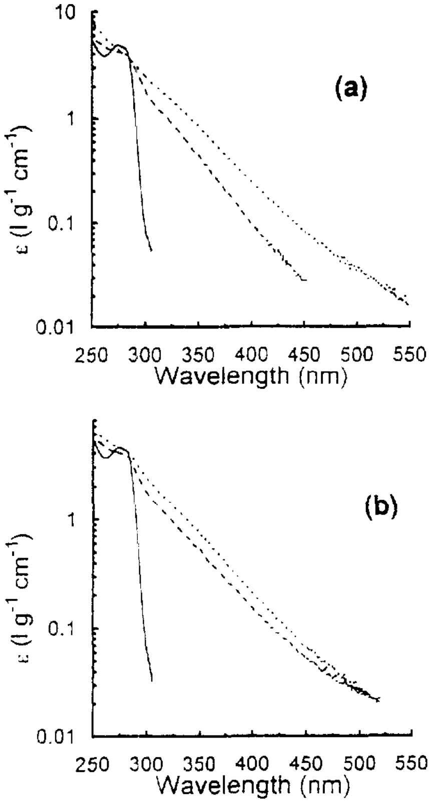
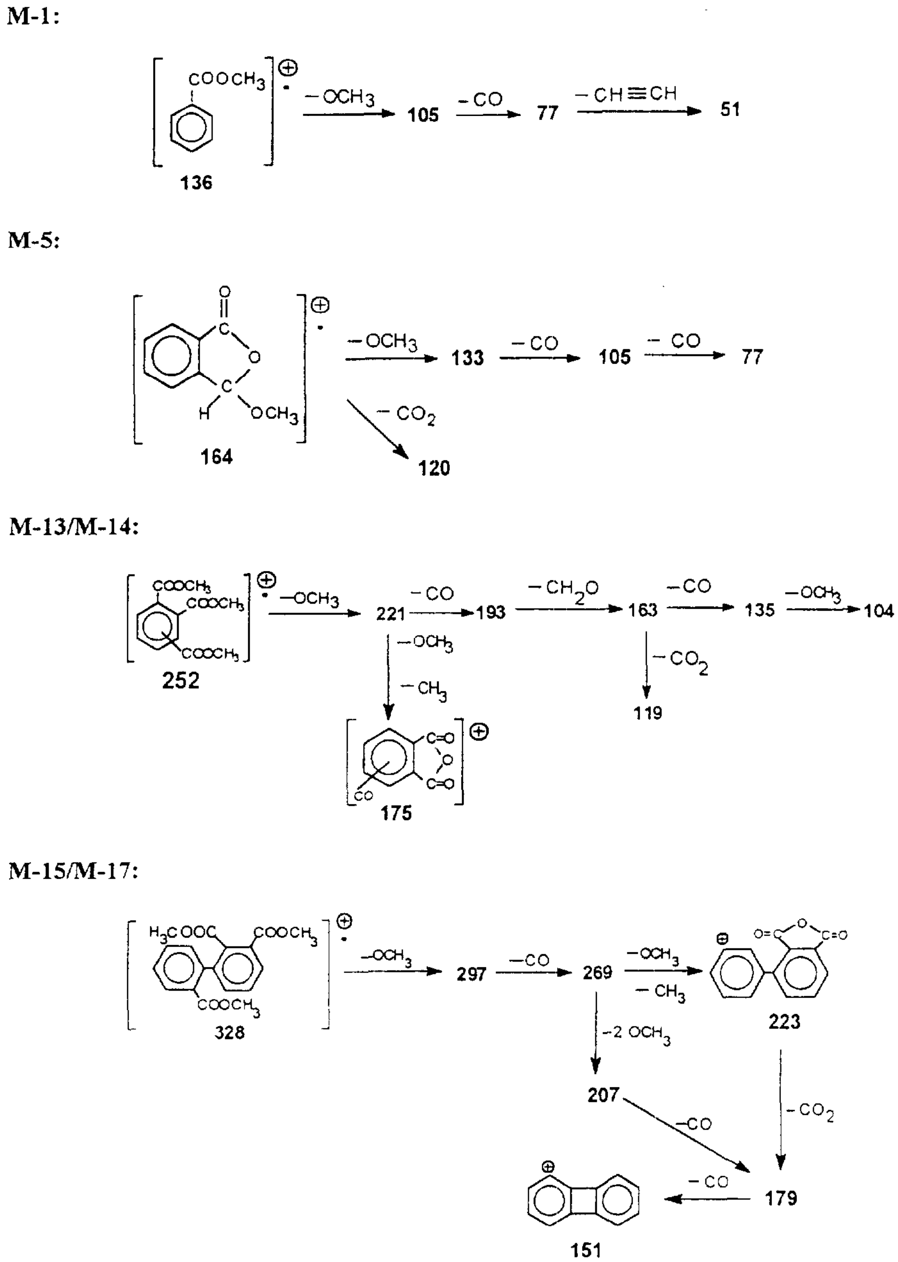


Fig. 4. UV absorption spectra recorded with methanol solutions of the ether-insoluble fraction generated in the photolysis of DMP (a) and DEP (b). (- - -) Subfraction extracted from the column with methanol/toluene (20:80, v/v); (...) subfraction extracted with methanol/toluene (80:20, v/v); (—) unirradiated neat phthalates.

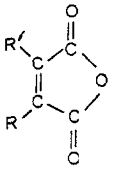
In conclusion, ^{1}H NMR spectroscopy reveals that the ether-insoluble fraction is characterized by a high degree of substitution at the aromatic rings and by the existence of a large number of aliphatic unsaturations.



Scheme 1. Mass spectral fragmentation patterns of the parent ions of compounds M-1, M-5, M-13/M-14 and M-15/M-17 formed in the photolysis of DMP. The bold numbers refer to *m/e* peaks of the corresponding mass spectra in Fig. 2.

3.2.4. IR absorption spectra

Fig. 7a shows IR spectra of unirradiated neat DMP and of two fractions of the ether-insoluble portion of the irradiated DMP. Taking the carbonyl band at 1729 cm^{-1} as an internal standard, it becomes obvious that the C–C bands at 1489, 1579 and 1600 cm^{-1} and the C–H band at 746 cm^{-1}, being characteristic of the benzene ring, and the bands at 1076, 1124 and 1286 cm^{-1}, being characteristic of the C–O vibration, are much weaker in the case of the irradiated material than in the case of unirradiated DMP. Moreover, the spectrum of the irradiated material contains new bands: one between 1630 and 1650 cm^{-1} which is attributed to the carbon–carbon double bond and a carbonyl band at about 1775 cm^{-1} (a shoulder) which is characteristic of an anhydride structure [11]:



From a comparison of the spectra a-2 and a-3, it is inferred that the spectrum of the fraction eluted with the methanol-rich binary solvent mixture (a-3) possesses new broad bands peaked at 1400 and 1614 cm^{-1} which are attributed to con-

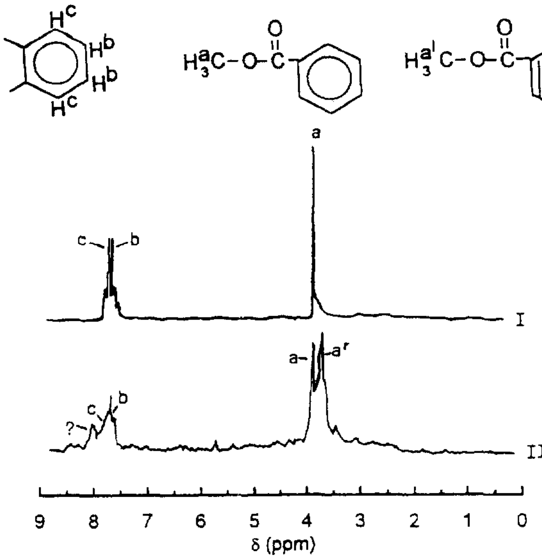


Fig. 5. ^{1}H NMR spectra recorded at 90 MHz with unirradiated neat DMP (I) and with the ether-insoluble fractions generated by photolysis of DMP (II).

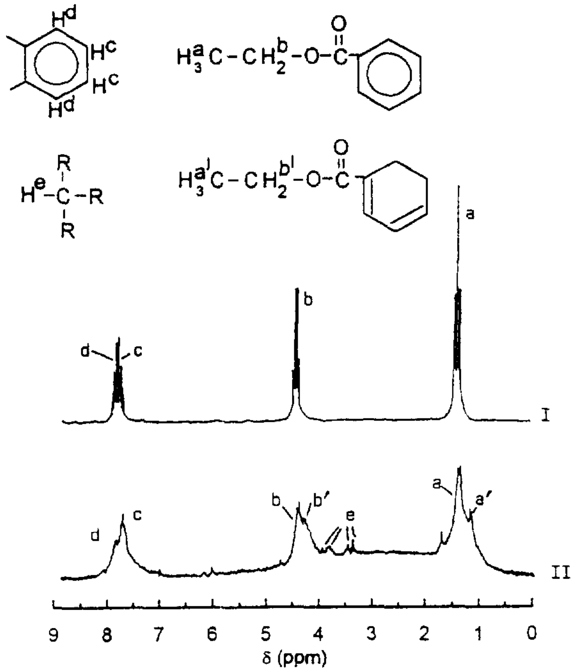


Fig. 6. ^{1}H NMR spectra recorded at 200 MHz with unirradiated neat DEP (I) and with the ether-insoluble fractions generated by photolysis of DEP (II).

jugated carbon–carbon double bonds, i.e., to structures containing polyene groups [12]. The IR analysis of the ether-insoluble portion of irradiated DEP (see Fig. 7b) yields similar results.

In conclusion, the IR measurements show that the content of aromatic rings and of ester groups is lower in the ether-insoluble portion of irradiated DMP and DEP than in the unirradiated neat phthalates, and that the ether-insoluble portions contain conjugated C=C double bonds.

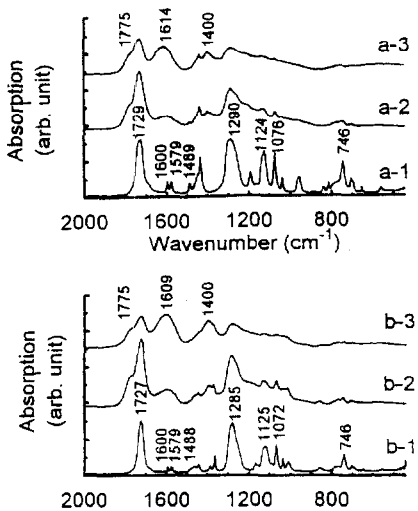
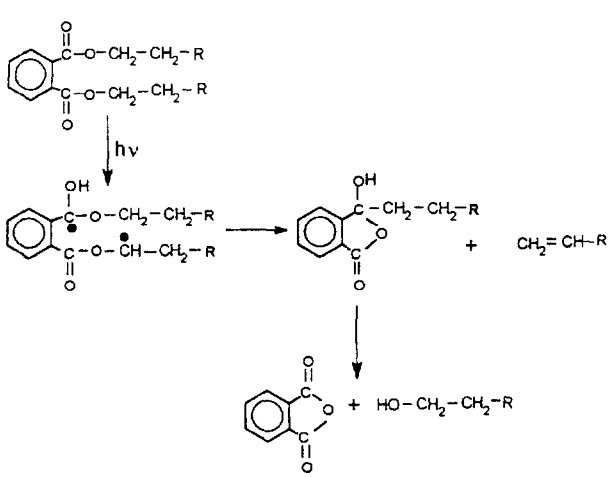


Fig. 7. IR absorption spectra recorded with unirradiated neat DMP (a-1) and DEP (b-1) and with the ether-insoluble fractions generated by photolysis of DMP (a-2, a-3) and DEP (b-2, b-3). Subfraction extracted from the column with methanol/toluene (20:80, v/v): (a-2, b-2). Subfraction extracted with methanol/toluene (80:20, v/v): (a-3, b-3).

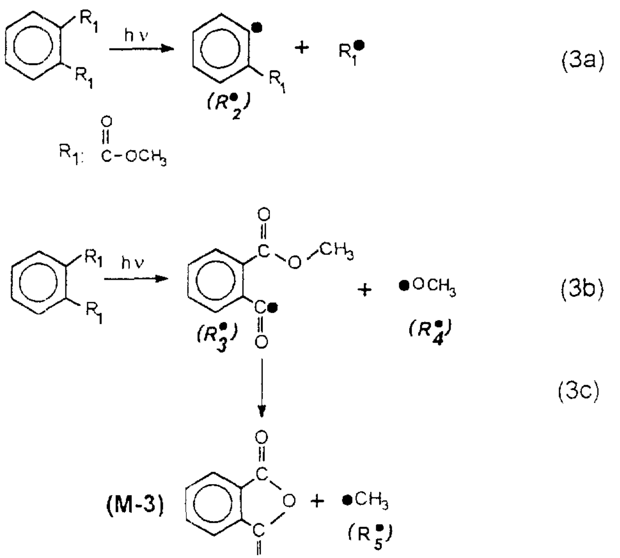
4. Discussion

4.1. Products contained in the low molar mass fraction

From the results of the product analysis, it can be inferred that the photolysis of DMP and DEP originates essentially from reactions involving the carbonyl groups. In this respect, DMP and DEP behave in the same manner as phthalates with alkyl groups containing many carbons. However, there are severe differences concerning the mechanism of reactions following the absorption of a photon by a carbonyl group. Whereas in the case of phthalates with large alkyl groups, intramolecular hydrogen abstraction essentially determines product formation (see Scheme 2) [1,6] scission of bonds next to the carbonyl chromophore appear to be most important for product formation in the cases of DMP and DEP. As can be seen from Scheme 3 referring to the photolysis of

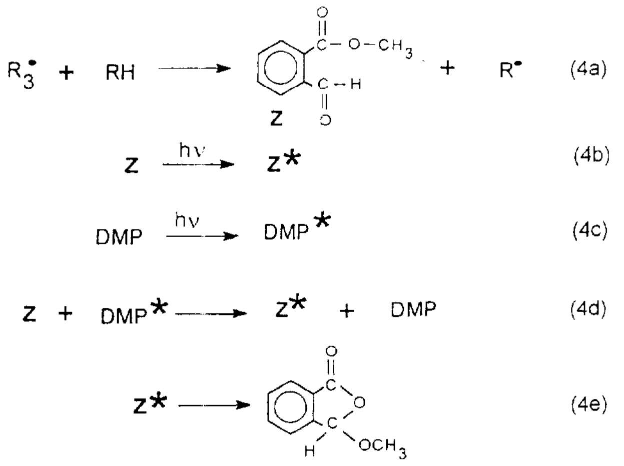


Scheme 2. Photoreactions of dialkyl phthalates with large alkyl groups.



Scheme 3. Generation of primary radicals in the photolysis of DMP.

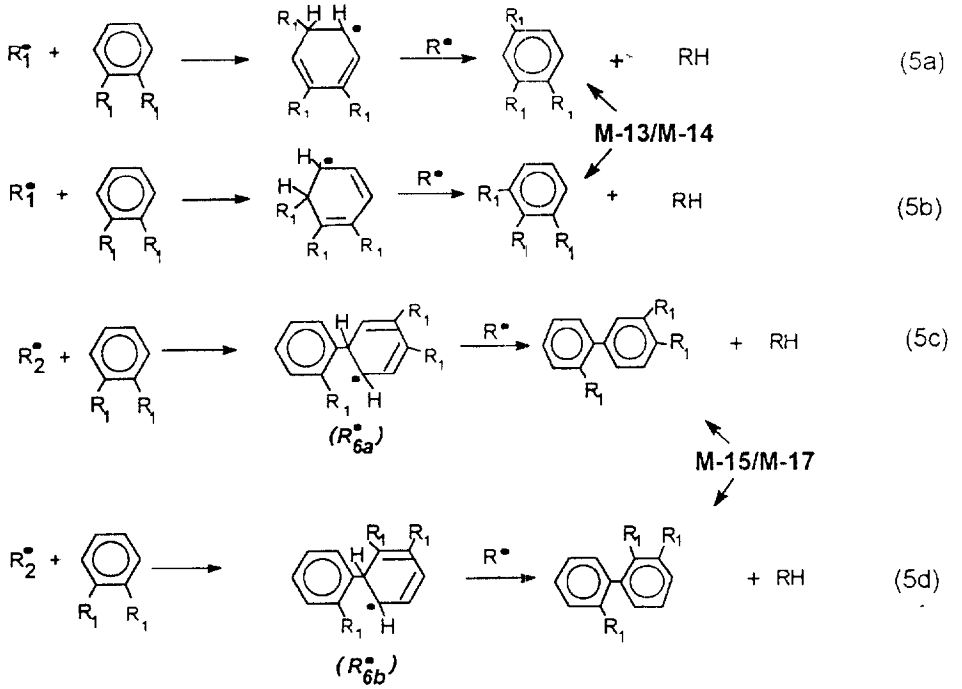
DMP, the cleavage of both the C–C bond connecting the COOCH$_3$ group to the benzene ring and the C–O bond (bond next to the carbonyl group) is feasible. In the former case, the radicals $R_1^{\cdot}$ and $R_2^{\cdot}$ (reaction 3a) and in the latter case the radicals $R_3^{\cdot}$ and $R_4^{\cdot}$ (reaction 3b) are formed. Radical $R_3^{\cdot}$ is likely to rearrange readily thus, forming phthalic anhydride and the methyl radical, $R_5^{\cdot}$. Alternatively, radical $R_3^{\cdot}$ may abstract a hydrogen from a surrounding molecule thus forming *o*-carbomethoxy benzaldehyde (2-formyl benzoic acid methyl ester) according to reaction 4a in Scheme 4. The latter compound as well as its analogue, *o*-carboethoxy benzaldehyde, expected to be formed in the photolysis of DEP, were not detectable. Nevertheless, there is good reason to assume that reaction 4a occurs. The evidence comes from the fact that the 3-alkoxy phthalides M-5 and E-4 are major products of the photolysis of DMP and DEP, respectively. Actually, the photolysis of *o*-carboethoxy benzaldehyde was reported to result largely in the formation of 3-ethoxyphthalide [9] and in the present cases the products M-5 and E-4 are very likely to originate from the photoisomerization of *o*-carbomethoxy and *o*-carboethoxy benzaldehyde, respectively, generated by type 4a reactions. Notably, the quantum yield of the isomerization is not known. But even if it is very large the photo-isomerization is unlikely to be due to direct photoexcitation of *o*-carboxy benzaldehyde (reaction 4b), since most of the incident light is absorbed by the phthalate (reaction 4c) and only a small fraction by the aldehyde. Therefore, the sensitized process depicted in Scheme 4 is proposed: the aldehyde (Z) undergoes an energy transfer reaction (4d) soon after its formation, and in this way the isomerization (reaction 4e) is induced. Because of the high rate constants of radical–radical reactions the formation of products via the combination of primary radicals including self-reactions is feasible. However, no evidence for the occurrence of self-reactions and of radical–radical reactions involving the radicals $R_1^{\cdot}$, $R_2^{\cdot}$, $R_3^{\cdot}$, $R_4^{\cdot}$ a and $R_5^{\cdot}$ was obtained. On the other hand, addition of radicals to the benzene ring of the phthalates seems to be of importance. In this way the formation of the isomer couples M-13/M-14 and M-15/M-17 can be explained. This is depicted by the mechanism presented in Scheme 5, which takes into account generally accepted features concerning the aromatic substitution involving free radicals [13]. Other clearly identified products cannot be traced back easily by a simple reaction mechanism involving primary radicals. This pertains, for example, to the photoproducts M-10 and E-6. In these cases, the mass spectra do not allow an assignment to the semi ester of *o*-phthalic acid and, therefore, a complicated not yet revealed mechanism, probably involving the reaction of esters of *m*- or *p*-phthalic acid is to be assumed.



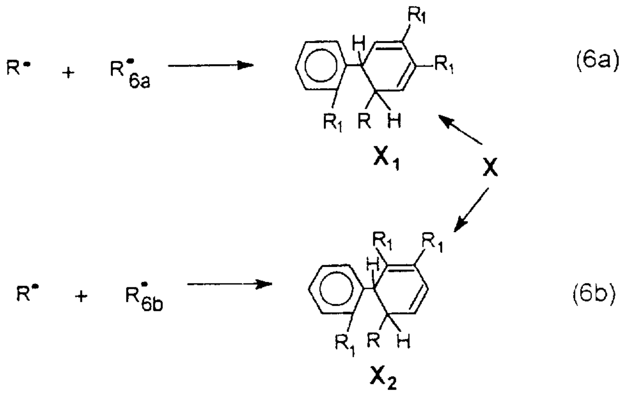
Scheme 4. Formation of product M-5.

4.2. Products contained in the high molar mass fraction

The ether-insoluble fraction consists of compounds of molar mass much higher than that of DMP or DEP, and of the photoproducts contained in the ether-soluble fraction. This is concluded from the size exclusion chromatograms presented in Fig. 3. Although the constituent parts of the ether-insoluble fractions could not be identified, it was inferred quite generally from the ^{1}H NMR and the optical absorption spectra that they are characterized by a high degree of substitution at the aromatic rings and by the existence of chromophoric groups absorbing light of rather long wavelength, very likely conjugated carbon–carbon double bonds. A possible pathway of the formation of molecules possessing such properties might involve radical combination reactions of $R_{6a}^{\cdot}$ and $R_{6b}^{\cdot}$ (see Scheme 6). Products such as X_1 and X_2, formed in this way, possess cyclohexadiene moieties that should be prone to undergo a ring-opening photo-rearrangement [14–21]. Hexatriene structures, generated by this process, could give rise (via free radical processes) to the formation of oligomeric products having a molar mass of



Scheme 5. Formation of products M-13/M-14 and M-15/M-17 via the addition of radicals $R_1^{\bullet}$ or $R_2^{\bullet}$ to DMP.



Scheme 6. Formation of product X_1 and X_2 via the reaction of radical $R^{\bullet}$ (kept unspecified) with radicals $R_{6a}^{\bullet}$ or $R_{6b}^{\bullet}$, respectively.

several 10^3 g mol^{-1} and possessing aliphatic unsaturations (conjugated carbon–carbon double bonds).

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