

## PHOTOLYSIS OF ETHYL $\alpha$ -CHLOROPHENYLACETATE IN CYCLO- HEXANE

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### Summary

Of many possible primary processes of photolysis of the compounds containing a carboxyl group, the primary reaction of ethyl  $\alpha$ -chlorophenylacetate (I) proceeds outside the carboxyl group and is in practice limited only to a homolytic C-Cl bond rupture.

Because of large differences in the rate of hydrogen abstraction by the  $\text{Ph}\dot{\text{C}}\text{HCOOEt}$  and Cl radicals, the main photolysis product of I in cyclohexane is  $\text{PhCH}(\text{C}_6\text{H}_{11})\text{COOEt}$  (II) and not  $\text{PhCH}_2\text{COOEt}$  (III) (as it was in the case of  $\alpha$ -haloesters).

Besides HCl and II, the other products of photolysis of I in cyclohexane are: III,  $\text{C}_6\text{H}_{11}\text{Cl}$  (IV), diethyl  $\alpha,\alpha$ -diphenylsuccinate ( $\text{PhCHCOOEt}$ )<sub>2</sub> (V), traces of *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COOEt (VI), as well as a number of secondary products, of which  $\text{PhC}(\text{C}_6\text{H}_{11})_2\text{COOEt}$  (VII) was identified. The quantum yields of main photolysis products are determined. The Norrish type II reaction does not play any significant role in the photolysis of I.

The excited singlet state of I is probably responsible for the C-Cl bond homolysis. The lifetime of this state has been estimated to be less than or equal to  $1 \times 10^{-11}$  s, and the quantum yield of fluorescence of I as  $< 1 \times 10^{-5}$ .

The photolysis of I is sensitized by benzene, and the products and quantum yields of sensitized photolysis are the same as in direct photolysis. The energy transfer takes place from the singlet state of benzene to the ester with the rate constant  $7.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

The mechanism of intramolecular energy transfer in I is considered.

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### Introduction

The mechanism of photolysis of esters  $\text{RCOOR}'$  differs considerably depending on the kind of R and R' substituents situated in the vicinity of their carboxyl group. In the case of aromatic derivatives, for instance, if  $\text{R} = \text{PhCH}_2-$ ,  $\text{R}' = \alpha$ - or  $\beta$ - $\text{CH}_2\text{Naph-}$ ,  $\text{PhCH}_2-$  (where Ph and Naph are, respectively, the phenyl and naphthyl groups), decarboxylation is the main primary photo-

lysis reaction [1, 2]. For aliphatic derivatives, when  $R = R' = \text{CH}_3(\text{Me})$ ,  $\text{C}_2\text{H}_5(\text{Et})$ ,  $\text{C}_3\text{H}_7(\text{Pr})$ , the ordinary Norrish type I and II reactions predominate [3]. In the latter case the mechanism of the primary processes changes considerably when the R substituent contains the halogen atom(s) (X) in the  $\alpha$ -position [4], whereas it does not change if X is in the  $\beta$ - or  $\gamma$ -position [5]. For  $R = -\text{CH}(\text{A})\text{X}$  (where  $\text{A} = \text{X}, \text{Me}$  and  $R' = \text{Me}, \text{Et}$ ) the C-X bond homolysis is the main primary process, while for  $R = -(\text{CH}_2)_n\text{X}$  ( $n = 2, 3$ ) and  $R' = \text{Me}, \text{Et}$ , C-X bond rupture is only a minor process compared to the  $\alpha$ -derivatives. The observed differences are due to a different character of the lowest excited states of the ester molecules [5]. On the other hand, the introduction to the haloester molecule of a phenyl group in the  $\alpha$ -position should also have a marked effect on the character of the lowest excited states of the ester and on the mechanism of photolysis of these compounds. Therefore we present here the results of photolysis of the simplest representative of this group, *i.e.* of (DL) ethyl  $\alpha$ -chlorophenylacetate (I) in cyclohexane ( $R = \text{PhCH}(\text{Cl})$ ;  $R' = \text{Et}$ ). Our investigations included qualitative and quantitative analyses of the main reaction products, determination of their quantum yields, as well as preliminary mechanistic studies concerning the multiplicity of excited states, sensitization effects, measurements of ester fluorescence, and the quenching of the benzene fluorescence. A comparison of these data for I with those obtained previously for aliphatic  $\alpha$ -haloesters, and also with unsubstituted ethyl phenylacetate (III) makes it possible to determine the differences in the mechanism of photolysis of these compounds and the origin of this photoreaction.

## Experimental

### Reagents

Ester I was synthesized from (DL) mandelic acid (Light, England) in two stages, first by its azeotropic esterification in the presence of  $\text{C}_2\text{H}_5\text{OH}$  and *p*-toluenesulphonic acid in  $\text{CCl}_4$ , and next by chloride substitution for the OH group in (DL)-ethyl mandelate by reaction with  $\text{SOCl}_2$  [6]. In the final stage of synthesis the ester was fractionally distilled under reduced pressure, collecting the fraction boiling at 134 - 136 °C/15 Torr. The structure of I was confirmed by spectral analysis (n.m.r., i.r., mass spectrum). The ester purity as determined by vapour-phase chromatography (v.p.c.) was  $\geq 99.5\%$ . Two other compounds were synthesized, *i.e.* ethyl  $\alpha$ -cyclohexylphenylacetate,  $\text{PhCH}(\text{C}_6\text{H}_{11})\text{COOEt}$  (II) and ethyl *p*-chlorophenylacetate (VI), which were obtained by esterification of respective acids (Fluka and Aldrich, respectively). The remaining compounds were analytically pure. Cyclohexane was additionally dried with anhydrous  $\text{MgSO}_4$ , distilled and stored over molecular sieves of the type 13 X (Serva, West Germany). A SilicAR CC-7 (Mallincrodt) silica gel was used.

*Preparative photolysis of ethyl  $\alpha$ -chlorophenylacetate (I)*

A solution of 1.345 g (6.78 mmol) of I in 60 ml of cyclohexane was placed in four quartz tubes and after 20 min of degassing with N<sub>2</sub> [7] was irradiated for 90 min in a "merry-go-round" reactor (MGR-100, Southern New England Ultraviolet Co.) using 15 RPR-2537 Å lamps. The course of the reaction was followed by v.p.c. using a Hewlett-Packard HP-5750 gas chromatograph with a TC detector (temperature programme: 100 °C for 4 min, then 20 °C/min, 255 °C for 10 min; columns: 0.125 in. × 6 ft, 10% UCW 98 on Chromosorb W 80 - 100 mesh, helium as carrier gas of the flow rate 2 l/h). Fast disappearance of the ester was observed (80%, v.p.c.). In addition to hydrogen chloride, appearance of the second, main photolysis product and four other products in much smaller amounts as well as traces of high-boiling products (which were absent at low conversions of I) was noted. The v.p.c. peak areas for the main photolysis products appeared in the ratio of 15:20:100:35:3 (in increasing order of retention times for products).

For isolation of acids which could form during photolysis, e.g., PhCH(Cl)COOH, PhCH<sub>2</sub>COOH and HCl, the combined photolysis solutions were extracted with 15% sodium hydroxide. The aqueous sodium hydroxide solution was then acidified with concentrated hydrochloric acid and extracted with ether. The ether was dried and evaporated leaving 14.7 mg (1.1%) of yellowish, solid residue insoluble in most solvents, and was shown not to contain any of the previously noted acids.

Cyclohexane was removed *in vacuo* to give 1.252 g of an oil. The two low-boiling photolysis products co-distilled with the solvent. They were identified by comparison of retention times of standards with the known compounds using a variety of v.p.c. columns. C<sub>6</sub>H<sub>11</sub>Cl (IV) and PhCH<sub>2</sub>COOEt (III) were identified as two of these products. The oil was analyzed first by t.l.c. and then separated on a silica gel column (2.5 × 75 cm, fraction volume 100 ml). Eluting with hexane gave in fractions 3 - 10, 35.0 mg (2.6% with respect to the amount of I used for irradiation) of III and 9.3 mg (0.7%) of the mixture of products with retention times longer than I; eluting with hexane and ether (99:1) gave in fractions 14 - 18, 486.2 mg (36.1%) of the mixture containing ≥90% of the main photolysis products identified as II (see below) and also 3% of ethyl  $\alpha$ ,  $\alpha$ -bicyclohexylphenylacetate, VII; eluting with hexane and ether (98:2) gave in fractions 19 - 32, 248.9 mg (18.5%) of the mixture containing mostly (~90%) the starting ester I and also VI (~3%); eluting with hexane and ether (96:4) gave in fractions 33 - 43, 243.5 mg (18.1%) of diethyl  $\alpha$ ,  $\alpha$ -diphenylsuccinate (V) (~90% purity); eluting with hexane and ether (94:6; 90:10; 80:20; 50:50) gave in fractions 44 - 49, 61 - 72, 73 - 77, and 78 - 80 a combined weight of 40.0 mg (3%) of the complicated mixture of many products which were not further analyzed; eluting with ether and finally with methanol gave in fractions 81 - 85 and 93 - 95, a total of 58.5 mg (4.3%) of the brown-yellowish, polymeric material.

Products II and VII from fractions 14 - 18 were additionally purified by g.l.p.c. and analyzed by n.m.r., mass and i.r. spectroscopy. For II the

following data were obtained: n.m.r. ( $\text{CCl}_4$ , TMS, 8 mg/0.4 ml; Varian TT 7 T 60)  $\delta$  7.25 (s, 5 H, phenyl), 4.06 (m, 2H,  $\text{CH}_2$ ), 3.10 (w, 1H, CH), 1.67 (broad) and 1.18 (s, 14 H,  $\text{C}_6\text{H}_{11}$ ,  $\text{CH}_3$ ); i.r. ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ): 3085, 3062, 3032 w; 2982 m, 2930, 2855 s, 1727 vs, 1600, 1493, 1474 w, 1445 m, 1387 w, 1367, 1328, 1297, 1283 m, 1269, 1252 w, 1235, 1220, 1190 m, 1153, 1125 s, 1092, 1070 w, 1028 m, 972, 948, 910, 892, 852 w, 700 s, mass spectrum  $m/e$  246;  $n_D^{20} = 1.522$ . Calculated for  $\text{C}_{16}\text{H}_{22}\text{O}_2$ : C, 78.00; H, 9.00%, Found: C, 77.79; H, 9.04%. The final assignment of II was done by comparison of its physical and spectral properties with an authentic sample from a separate synthesis. Assignment of VII was made from the i.r. and mass spectra; i.r. ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ): 2974 w, 2928, 2852, 1726 s, 1505 w, 1443 m, 1416, 1386, 1363, 1345, 1325, 1287, 1265, 1251, 1231, 1215, 1183 w, 1152 s, 1122 m, 1094 w, 1030 m, 1020, 995, 970, 888 w; mass spectrum,  $m/e = 328.2425$ , calcd. 328.2402 by peak matching. Product V from fractions 33 - 43 was also purified by g.l.p.c., recrystallized and sublimed giving white crystals of m.p. 139 - 140 °C (lit. 140 - 141 °C for *meso* form of V [8]), n.m.r. ( $\text{CDCl}_3$ , TMS)  $\delta$  7.33 (10 H, 2  $\times$  phenyl), 4.37 (2H, 2  $\times$  CH), 3.85 (4 H, 2  $\times$   $\text{CH}_2$ ), 0.92 (6 H, 2  $\times$   $\text{CH}_3$ ); i.r. ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ): 3107, 3082, 3050 w, 3000, 2948, 2870 s, 1730 vs, 1605 w, 1500 m, 1480 w, 1460 m, 1395 w, 1374 s, 1345, 1330 w, 1305, 1290 s, 1226 m, 1205 w, 1153 vs, 1100, 1080 w, 1035 s, 953, 919, 900, 870, 856 w, 700 s; mass spectrum  $m/e = 326.1514$ , calcd. 326.1517 by peak matching. All other compounds (I and VI) were identified by comparison of v.p.c. retention times with known samples.

The following spectrometers were used: n.m.r., Varian E-360; i.r., Beckman Acculab-3, Unicam SP-200 G, UV, Specord, VSU-2P (Zeiss); mass, Varian MAT CH-5, JEOL JMS D-100. Elemental analyses were carried out using Hewlett-Packard 185 B analyzer.

#### Quantum yield ( $\Phi$ ) determination

A solution of the ester I and cyclodecane (as an internal standard) in 4 ml of cyclohexane in a quartz tube was degassed with argon, placed in a merry-go-round apparatus [4] and irradiated at 20 °C with nearly monochromatic 254 nm radiation from a TNN - 15/32 low-pressure mercury vapour lamp (Original-Hanau, West Germany). Light output was monitored by uranyl oxalate actinometry. Samples were withdrawn at intervals and analyzed directly by v.p.c., using a PYE 104 gas chromatograph equipped with flame ionization detector (programme: 90 °C for 4 min, then 17 °C/min, 240 °C for 15 min, columns: 0.25 in.  $\times$  6 ft, 3% OV - 17 on Gas Chrom Q, nitrogen as carrier gas of the flow rate 3 l/h).

HCl was determined separately by potentiometric titrations [9].

#### Sensitization and quenching experiments of the photolysis of I

Benzene sensitization of the photolysis of I was investigated at  $\lambda \approx 254$  nm in cyclohexane, using the merry-go-round unit described above ( $\Phi$ -values determinations). Quenching experiments were performed with *cis*-1,3-pentadiene (Fluka,  $\geq 99\%$ ) also at  $\lambda \approx 254$  nm in cyclohexane. Sensi-

tizer concentrations were sufficient to capture  $\geq 95\%$  of the incident light. Concentrations of the quencher were adjusted so that capture of incident light was less than 5%. Before irradiation, samples with and without sensitizers were degassed with argon, and analyzed at intervals. Products and ester concentrations were followed by v.p.c. using cyclodecane as an internal standard. The data were normalized so that the light input to I in all samples of the different concentration of the quencher was assumed to be the same.

### *Fluorescence measurements*

Fluorescence measurements were performed in 1 cm quartz cells with an Aminco-Bowman spectrofluorimeter and later, for determination of the quantum yield of fluorescence ( $\Phi_f$ ) with a Perkin-Elmer MPF-3 spectrofluorimeter, equipped with a spectra correction attachment. The emission spectrum of I was measured at its various concentrations in cyclohexane and n-pentane, corresponding to the absorbances within the range 0.01 - 2.0, at optimum slits and sensitivities of the apparatus. Under such conditions no measurable fluorescence of I was found. In order to determine the minimum  $\Phi_f$  value measurable under the same conditions, comparative studies were performed, using benzene as a fluorescence standard ( $\Phi_f = 0.05$  [10]). Concentrations of I and of the standard were adjusted in such a way that at  $\lambda_{exc} \approx 254$  nm the absorptions of the systems were the same. In these conditions it was possible to determine the minimum  $\Phi_f$  value by comparing the corrected benzene emission spectra with those of the investigated compound.

In the case of quenching of benzene fluorescence by I the concentrations of benzene and of the ester were chosen in such a way that the ester did not absorb more than 5% of exciting radiation at  $\lambda \approx 254$  nm. This competitive absorption of the ester was taken into account in calculating the value of the Stern-Volmer plot which described the quenching of benzene fluorescence.

## Results

### *Absorption spectrum of I*

The data concerning the absorption spectrum of I in cyclohexane are collected in Table 1. In order to compare the effect on the electronic spectra of an  $\alpha$ -halogen atom with that of an unsubstituted ester (ester III), this Table also contains similar analytical data for benzyl chloride ( $\text{PhCH}_2\text{Cl}$ ) and III.

The spectrum of I differs considerably from absorption spectra of either III or  $\text{PhCH}_2\text{Cl}$ . Apart from a considerable increase in the absorption below 250 nm, a notable broadening and increase in intensity of the band connected with the  $\pi, \pi^*$ -type transition in the phenyl group for I is observed. For comparison, Fig. 1 shows the absorption spectra of I and the equimolar mixtures of  $\text{PhCH}_2\text{Cl} + \text{CH}_3\text{COOEt}$  and  $\text{PhH} + \text{ClCH}_2\text{COOEt}$  in cyclohexane. Spectra of these mixtures (II and III) do not differ appreciably from those of pure  $\text{PhCH}_2\text{Cl}$  and benzene, respectively.

TABLE 1

Molar absorptivities ( $\alpha$ ) and absorption maxima ( $\lambda_{\max}$ ) of esters I, III and benzyl chloride in cyclohexane.

Compound	$\lambda_{\max}$ (nm)	$\alpha_{\max}$ ( $M^{-1} \text{ cm}^{-1}$ )	$\alpha_{254}$ ( $M^{-1} \text{ cm}^{-1}$ )
PhCH(Cl)COOEt (I)	260	371	
	266	314	448
	272	198	
PhCH <sub>2</sub> COOEt (III)	248	115	
	253	142	
	259	176	142
	265	136	
PhCH <sub>2</sub> Cl	255	167	
	261	210	
	267	190	167
	272	108	

$\alpha_{\max}$  and  $\alpha_{254}$  = molar absorptivities at  $\lambda_{\max}$  and at  $\lambda = 254$  nm, respectively.

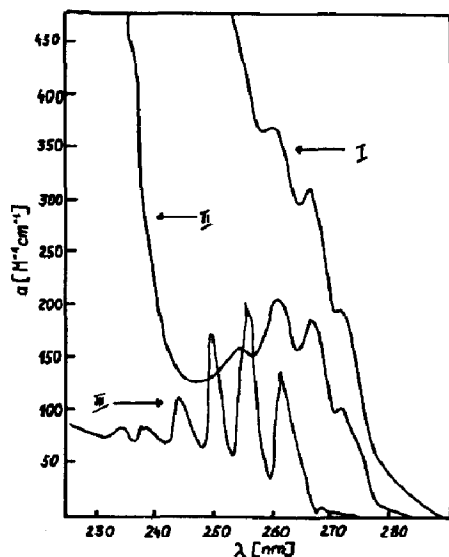


Fig. 1. The absorption spectra in cyclohexane: I, PhCH(Cl)COOEt; II, equimolar mixture of PhCH<sub>2</sub>Cl + CH<sub>3</sub>COOEt; III, equimolar mixture of PhH + ClCH<sub>2</sub>COOEt.

### Direct and benzene-sensitized photolysis of I

The quantum yields  $\Phi$  for disappearance of I and for appearance of the main products of photolysis are presented in Table 2. It has been found that benzene sensitizes the photolysis of I and the products of sensitized photolysis do not differ from those obtained from direct irradiation. The process of de-aeration of the system prior to irradiation had no effect on the  $\Phi$  values both in the case of direct and sensitized photolysis.

TABLE 2

Quantum yields<sup>a</sup> of main products of direct and sensitized by benzene photolysis of ethyl  $\alpha$ -chlorophenylacetate (I) in cyclohexane at  $\lambda \approx 254$  nm.

Photolysis products	Direct photolysis	Benzene sensitized photolysis <sup>b</sup>
disappearance of I	0.55 $\pm$ 0.13	0.53 $\pm$ 0.13
HCl	0.51 $\pm$ 0.05 <sup>c,d</sup>	0.52 $\pm$ 0.05 <sup>c,d</sup>
	0.50 $\pm$ 0.05 <sup>d</sup>	0.52 $\pm$ 0.05 <sup>d</sup>
PhCH(C <sub>6</sub> H <sub>11</sub> )COOEt (II)	0.26 $\pm$ 0.06	0.22 $\pm$ 0.06
(PhCHCOOEt) <sub>2</sub> (V)	0.08 $\pm$ 0.03	0.07 $\pm$ 0.03
C <sub>6</sub> H <sub>11</sub> Cl (IV)	0.04 $\pm$ 0.02	0.05 $\pm$ 0.02
PhCH <sub>2</sub> COOEt (III)	0.04 $\pm$ 0.02	0.04 $\pm$ 0.02

<sup>a</sup> Values obtained from extrapolation of the results of several runs at different % conversion to 0% conversion, mean light input, ( $LI$ ) =  $(2.8 \pm 0.3) \times 10^{-2}$  mE h<sup>-1</sup> cm<sup>-3</sup>.

<sup>b</sup> Benzene concentration 6.2 M, benzene capture  $\geq 95\%$  of 254 nm radiation.

<sup>c</sup> Samples after deaeration before irradiation [7].

<sup>d</sup> ( $LI$ ) =  $(3.2 \pm 0.3) \times 10^{-2}$  mE h<sup>-1</sup> cm<sup>-3</sup>.

At high conversion of I a number of other products appeared in small amounts (see preparative photolysis) out of which VI and VII were identified. The quantum yield of VII increased with the increase of the conversion of I, which indicates that it is probably the product of secondary photolysis.

#### Photolysis of I in the presence of *cis*-1,3-pentadiene

In order to obtain information concerning the excited state of ester I responsible for the observed reactions, the photolysis of I was performed in the presence of *cis*-1,3-pentadiene (piperylene, Q) [3]. The molar absorption coefficient of I ( $a_{254} = 448$ ) and of the applied diene ( $a_{254} = 20$ ) allowed the use of piperylene over relatively large concentration range (0.001 - 1.2 M) where I absorbed  $\geq 95\%$ . The higher concentration range of Q made it possible to investigate the quenching of short-lived triplet states as well. However, complications which are likely to accompany the use of olefins and dienes as the quenchers of the excited states [5, 11b, c], including those with the radical reactions occurring with participation of the quencher [11a], were unavoidable. Attempts were made to overcome this by observing and correlating the  $\Phi$  changes of both the substrate disappearance and the appearance of the reaction products.

It was found that within the concentration range 0.001 - 0.1 M, Q had practically no effect on either the quantum yields of the appearance of HCl and other main photolysis products or the disappearance of I. For concentrations of Q  $\geq 0.2$  M, however, the effect on the  $\Phi$  values was different for different products of photolysis and for the disappearance of I, as illustrated in Table 3.

These data clearly show that *cis*-1,3-pentadiene can exhibit not only a physical quenching of the excited state, but also chemical quenching of the photoproducts of I, either by scavenging the free radicals formed or by formation of photo-adducts [12]. Chemical quenching was confirmed by the

TABLE 3

The slopes<sup>a</sup> ( $k_q\tau$ ) of the Stern–Volmer plot describing changes of  $\Phi$  values for disappearance of I and formation of products with increasing *cis*-1,3-pentadiene (Q) concentration, in cyclohexane, at  $\lambda \approx 254$  nm.

Photolysis product	$k_q\tau$ ( $M^{-1}$ )
disappearance of I	-0.1
HCl	0.1
PhCH(C <sub>6</sub> H <sub>11</sub> )COOEt (II)	4.2 <sup>b</sup>
PhCH <sub>2</sub> COOEt (III)	3.5 <sup>b</sup>
C <sub>6</sub> H <sub>11</sub> Cl (IV)	28 <sup>b</sup>

<sup>a</sup>Calculated using least square method, after taking into account the competitive absorption of *cis*-1,3-pentadiene at 254 nm.

<sup>b</sup>Determined from the linear portion of Stern–Volmer plot in the *cis*-1,3-pentadiene concentration range from 0.2 to 0.6 M.

appearance at large concentrations of Q, of a number of new compounds which were absent during photolysis of I and Q performed separately. Furthermore, if the physical quenching of I were the only function of the quencher, the Stern–Volmer plot for both the disappearance of substrates and appearance of each product would be the same, assuming a single reactive excited state. Their different values (Table 3) point rather to different rates of scavenging of radicals Ph $\dot{C}HCOOEt$ ,  $\cdot C_6H_{11}$  and Cl by Q.

#### Fluorescence of I: quenching of benzene fluorescence by I

The relative quantum yield ( $\Phi_f$ ) of ester I fluorescence is  $\Phi_f < 1 \times 10^{-5}$ \*. The  $\Phi_f$  value measured under the same conditions for ester III is 0.05, which is in agreement with earlier observations [15], where it was determined as approximately equal to 30% yield of  $\Phi_f$  of toluene used as a standard ( $\Phi_f = 0.14$  [10]).

In order to establish the involvement of the benzene singlet state in the process of energy transfer from the sensitizer to the ester I, investigations were performed on the quenching of benzene fluorescence by I. It was found that I could quench the benzene fluorescence effectively, and that the unquenched portion of this fluorescence had the same spectral distribution as the system in the absence of quenchers. However, the rate constant of the quenching of benzene fluorescence  $k'_q$  by I differs considerably from those

\*Knowing  $\Phi_f$  and the radiative lifetime  $\tau_f$  one could determine the lifetime  $\tau_s$  of state  $S_1$  of the molecule of I from the equation:  $\tau_s = \Phi_f \tau_f$ . The usual estimation of  $\tau_f$  values from the integration of the longest wavelength absorption band [13] is impossible for I, as this band is buried to a large extent by a more intense band of  $\lambda_{max} = 221$  nm ( $\alpha > 5000$ ). However, assuming  $\tau_f$  as equal to  $1 \times 10^{-7} - 1 \times 10^{-8}$  s, a value characteristic of most known aromatic derivatives containing the benzene ring [14], the  $\tau_s$  value can be approximately estimated as  $< 1 \times 10^{-12} - 1 \times 10^{-13}$  s.



for aliphatic haloesters [5]. This constant was determined from the Stern-Volmer equation:

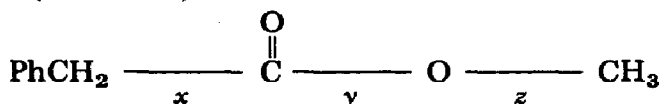
$$\frac{\Phi'_0}{\Phi'_Q} = 1 + k'_q \tau_b [Q']$$

where  $\Phi'_0$  and  $\Phi'_Q$  are quantum yields of benzene fluorescence in the absence and presence, respectively, of the ester of concentration  $[Q']$ , and  $\tau_b$  is the lifetime of the benzene singlet excited state.

For ester I the  $k'_q \tau_b$  value obtained was  $855 M^{-1}$ , as compared with, for instance, a similar value for  $\text{ClCH}_2\text{COOEt}$  of  $10.2 M^{-1}$ . Moreover, assuming a  $\tau_b$  value of 12.2 ns [16], a calculated  $k'_q$  value of  $7.0 \times 10^{10} M^{-1} s^{-1}$  for I, and  $8.4 \times 10^8 M^{-1} s^{-1}$  for  $\text{ClCH}_2\text{COOEt}$  [5] was obtained.

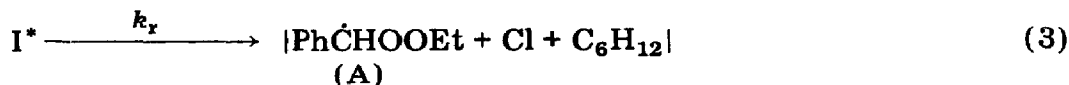
## Discussion

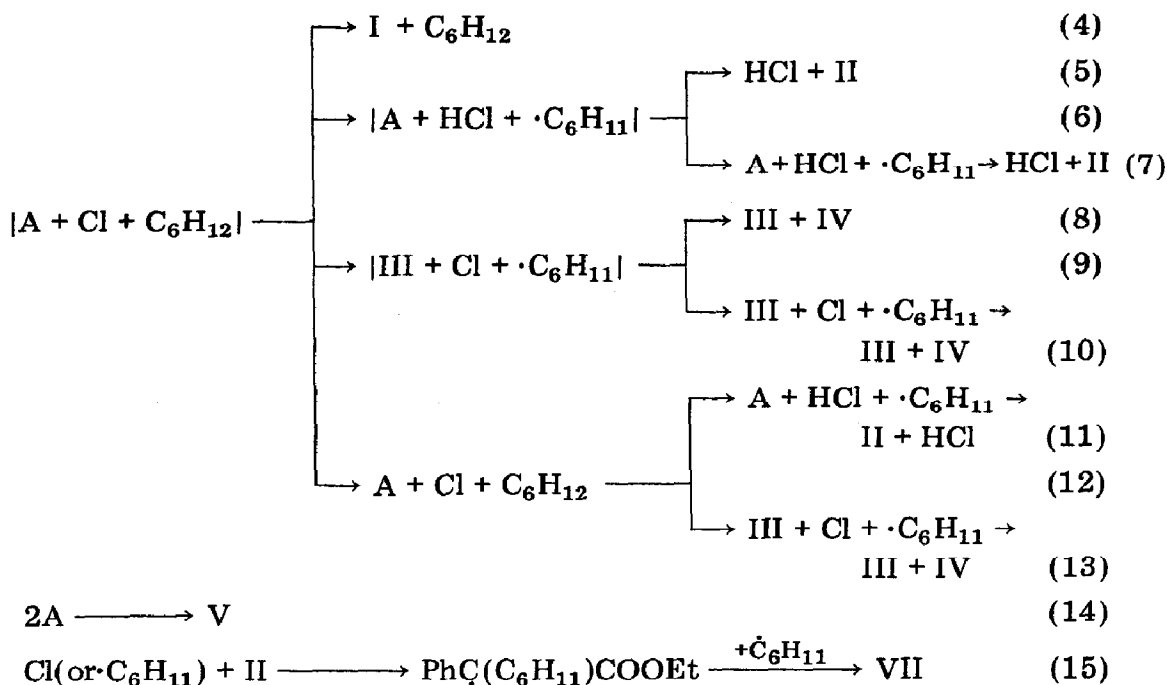
Out of 25 hypothetical primary processes of photolysis, which a compound with the carboxyl group can undergo, as reported by Meiggs and Miller [17], only about a half have been confirmed experimentally. In this context the primary processes of photolysis of ester I are very simple. The results indicate that the introduction of an  $\alpha$ -chlorine into III considerably affects the photochemical processes for this molecule. The primary reactions of photolysis of I differ considerably in comparison with ester III. For the latter compound (its methyl derivative) they are limited to the carboxyl group only and consist in  $x$  and  $y$  bond rupture with low quantum yield values ( $\Phi < 0.03$ ).



Here, the  $y$  bond rupture is the dominating process [17]. In contrast to ester III, the main and practically the only primary reaction of photolysis of I, occurring with high quantum yields ( $\Phi_{\text{ester disapp.}} \sim 0.5 - 0.6$ ), is the C-Cl bond rupture.

The reaction scheme shown below illustrates the course of photolysis of I in cyclohexane:





where  $| |$  denotes the radical "cage",  $h$  is Planck's constant,  $\nu$ , frequency of exciting radiation,  $A$ ,  $Ph\dot{C}HOOEt$  radical, and  $k_d$ , the sum of the rate constants of both radiative and non-radiative processes proceeding from the excited state of  $I^*$ , and different from the chemical reaction (of the C-Cl bond homolysis) proceeding from that state. The rate constant of the latter process has been denoted as  $k_r$ .

Before discussing the identity of excited state of  $I^*$  which is responsible for the observed reactions, analysis of the experimental data reveals that the reactions of the excited state of  $I$  are associated with homolytic C-Cl bond rupture giving  $A$  radicals and the  $Cl$  atoms, which was also previously observed for a series of aliphatic  $\alpha$ -haloesters [4]. The hydrogen abstraction from the solvent molecules by  $A$  radicals and  $Cl$  leads to the appearance of the main products,  $HCl$  and  $III$ . However, in contrast to aliphatic  $\alpha$ -haloesters,  $II$  (and not  $III$ ) becomes the major organic product of photolysis of  $I$ . This is probably due to large differences in the rate of hydrogen abstraction from the solvent molecules by aromatic radicals in comparison with aliphatic radicals. For instance, in contrast to methyl radicals the rate of hydrogen abstraction from hydrocarbons by the benzyl radicals ( $Ph\dot{C}H_2$ ) is negligibly small [17, 18]. This is also indicated by the products of  $PhCH_2Cl$  photolysis in vapour state in the presence of  $C_2H_6$  and  $n-C_4H_{10}$  [19]. At the same time the rate of hydrogen abstraction by the  $Cl$  atoms from hydrocarbons is quite large [20], which leads to a high concentration of cyclohexyl radicals formed mainly in reactions (6) and (11). Moreover, recombination of these radicals with  $A$  [processes (5), (7) and (11)], and also of two  $A$  radicals (reaction 14), affords the main organic photolysis products  $II$  and  $V$ .

Reaction (14) does not play any significant role in the photolysis of  $\alpha$ -monohaloesters [4, 21]. A large yield of II, ( $\sim 39\%$ ) isolated after photolysis, in comparison with the amount of I which was converted, indicates that the photolysis of I might be used to obtain preparatively a series of  $\alpha$ -derivatives of phenylacetate esters, by using the good hydrogen donating solvents.

The appearance of ester VII at higher conversion of I is associated with the secondary reactions proceeding in the system (see above). Abstraction of tertiary hydrogens by Cl is highly favoured kinetically [22], particularly, when there is the phenyl group in the  $\alpha$ -position [20 c]. In turn, the combination of the product radical,  $\text{Ph}\dot{\text{C}}(\text{C}_6\text{H}_{11})\text{COOEt}$ , with  $\cdot\text{C}_6\text{H}_{11}$ , results in the appearance of VII (reaction 15).

It is very difficult to determine unequivocally the role of the "cage" effect during the formation of the reaction products, owing to a large variety of the possible radical reactions proceeding in the system\*. This has been recently determined quantitatively for the main product of photolysis, of  $\beta$ -naphthalene phenylacetate [23] by using the ester specifically labelled with deuterium. The high  $\Phi$  of the formation of V (reaction 14), which can form only as a result of recombination of A-radicals outside the solvent "cage", indicates that at least some part of product V is formed in reactions (7) and/or (11).

A radicals and Cl in the solvent "cage" can also recombine, which leads to regeneration of the initial ester (reaction (4)). This process, which is tantamount to non-radiative decay of  $\text{I}^*$  in the chemical way, has been included in the scheme with reaction (2) for two reasons. (a) The mechanism of non-radiative decay of state  $\text{I}^*$  is unknown. Both the  $\Phi_f$  values measured here for  $\text{I} < 1 \times 10^{-5}$ , and  $\Phi_{\text{disapp.}}$  of  $\text{I} = 0.55 \pm 0.13$ , as well as the lack of any other chemical routes from the state  $\text{I}^*$  show that the real involvement of reaction (3) in the deactivation of  $\text{I}^*$  can be larger than it appears from the measured value of  $\Phi_{\text{disapp.}}$  of  $\text{I}^\dagger$ . The "cage" effect similar to reaction (4), has recently been confirmed experimentally. Also quantum yields of radicals recombination in the "cage" have been determined [23]. (b) The quantum yield of the disappearance of I was found to increase with the increase of the *cis*-1,3-pentadiene concentration (Table 3). This results in the negative value of the slope of the Stern-Volmer plot for the disappearance of I. At a concentration  $Q = 1.2 \text{ M}$ ,  $\Phi_{\text{disapp.}}$  of I increases from 0.55 up to 0.63. The role of the diene with large concentrations in the system may consist in the scavenging of

\*The application of optically active ester I and analysis of optical activity of the main product IV (isolated from the reaction mixture) as well as of I, could give some additional information concerning the role of the "cage" effect in formation of the product, and also in reaction (4).

†The decrease of the  $\Phi_f$  values in going from III ( $\sim 0.05$ ) to I ( $< 1 \times 10^{-5}$ ) is connected with the increase (in comparison with III [17]) of the rate of chemical reactions proceeding probably from the singlet state of I, although it may also be due to the increase  $\Phi$  of intersystem crossing in I [15]. The lack of data concerning this value as well as the  $\Phi$ -value of radicals recombination (reaction 4) additionally complicates quantitative determination of the involvement of reaction (2) in the process of decay of  $\text{I}^*$ , although it seems that this process should not play any significant role here [15].

radicals forming in reaction (3)\* which in turn, results in the increase of  $\Phi_{\text{disapp.}}$  of I by decreasing the participation of reaction (4).

A comparison of quantum yields of the disappearance of I with those of the appearance of products (Table 2) show that: (a)  $\Phi_{\text{disapp.}}$  of I is approximately equal to  $\Phi_{\text{Cl}}$  of the appearance of Cl-containing products ( $\Phi_{\text{Cl}} = \Phi_{\text{IV}} + \Phi_{\text{HCl}} = 0.54 \pm 0.07$ ) and A radical-containing products ( $\Phi_{\text{A}} = \Phi_{\text{II}} + 2\Phi_{\text{V}} + \Phi_{\text{III}} = 0.46 \pm 0.14$ ) confirming that the C-Cl bond homolysis (reaction 3) is practically the only chemical reaction of I\* (the secondary products, which have been found in small amounts at high conversions, appear either as a result of reactions similar to reaction (15), or in effect of other radical reactions with participation of both the substrate and the products of photolysis of I); (b) the participation of type I Norrish reactions similar to those observed during photolysis of PhCH<sub>2</sub>COOMe [17] is negligible in the case of I. The lack of PhCH(Cl)COOH in the reaction products also points of the lack of type II Norrish reactions for this compound.

Although the information concerning the character of the excited states responsible for the photolysis of simple ester derivatives of phenylacetic acid is scarce [1, 17], the data available for other ester derivatives of this acid, indicate that the singlet state of these compounds plays a major role [2, 25 - 27]. From the quenching experiments with *cis*-1,3-pentadiene it can be seen that  $\Phi_{\text{disapp.}}$  of I does not decrease even at a concentration  $Q = 1.2 M$ . At the same time  $\Phi_{\text{HCl}}$  slightly decreases (Table 3). These data allow estimation of the maximum lifetime of the reactive excited state of I\* to be  $\leq 1 \times 10^{-11}$  s. Thus, I\* is most likely a singlet state. The short lifetime can also be accounted for by the lack of the oxygen effect in the system on the  $\Phi$  values (Table 2). In addition, I can be sensitized by benzene. The energy transfer occurs from the singlet state of benzene to I, which is evidenced by effective quenching by I of benzene fluorescence. A considerable broadening and increase in intensity of the absorption band of I in comparison with the sensitizer (benzene), also observed in many other benzene derivatives, and the decrease in energy of the lowest S<sub>1</sub> state [14] suggest, that the energy of the S<sub>1</sub> state of I is considerably lower than that of benzene (110 kcal/mol [10]). In such a case the exothermic energy transfer of the type singlet (benzene) → singlet (ester) is very probable. The products as well as quantum yields of singlet sensitized photolysis are the same as in direct photolysis<sup>†</sup> which is evidence that it proceeds in both cases from the same state.

The mechanism of energy transfer from benzene S<sub>1</sub> state to haloesters differs in the case of I from that of the aliphatic haloesters [5]. This is evidenced particularly by considerable differences observed in the rate cons-

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\*The rate constants of Cl-addition to the double bond for a series of olefins are much higher than those of hydrogen abstraction [24].

†This is especially worth emphasizing, as in the case of large benzene concentrations in the system ( $> 6 M$ ), the concentration of some radicals (Cl) in the hydrogen abstraction reaction from cyclohexane can be much lower owing to the possibility of formation of  $\pi$ -complexes between Cl-atoms and the benzene molecule [28].

tants for quenching of benzene fluorescence by I ( $k'_q = 7.0 \times 10^{10} M^{-1} s^{-1}$ ), as compared with, *e.g.*  $ClCH_2COOEt$  ( $k'_q = 8.4 \times 10^8 M^{-1} s^{-1}$ ). Most probably in the latter case the energy transfer takes place through the formation of an excited complex between the benzene molecule in the  $S_1$  state and the ground state ester [5]. Apart from a much smaller  $k'_q$  value in comparison with I this is additionally confirmed by a decrease of the  $\Phi$  value of the benzene-sensitized photolysis of  $ClCH_2COOEt$  (see below), which is probably connected with reversibility of formation of the complex discussed earlier. The attempts to correlate the rate constants of  $k'_q$  with ionization potentials of various donors and electron affinities of the acceptors (haloesters), in order to ascertain the nature of the complex, are the subject of current investigations.

Finally, the question remains as to how the 112.7 kcal/mol of radiant energy is localized in the ester molecule. Is it the intramolecular energy transfer from one of the chromophores (*e.g.* of the phenyl or carboxyl group) to the C-Cl group that is responsible for the observed reactions, or is the absorption of radiation by I connected with the delocalized excitation of the whole molecule leading directly to the C-Cl bond homolysis? In the case of photolysis of phenylacetic acid esters, this problem focused the attention of many authors [2, 15, 26, 27]. A comparison of absorption spectra, presented in the experimental section (Table 1 and Fig. 1), shows that in the case of I there exists interaction between the phenyl group and the carboxyl group, increased in comparison with III [15] owing to the presence of the C-Cl bond in the  $\alpha$ -position. This means that the chromophores lose their identity in I, and that in this case a complex chromophore, resulting from interactions among the three groups, is probably responsible for absorption of radiation. A similar effect was observed in other esters, derivatives of phenylacetic acid [15, 26, 27]. Thus, the process of absorption of radiation should rather be treated as the absorption connected with delocalization of excitation over the whole molecule. The electronic state which appears as a result of such an excitation, differs in its characteristics from the states resulting from  $n, \pi^*$ ,  $\pi, \pi^*$ , and  $n, \sigma^*$  transitions for independent chromophores. The formation of a new, mixed state from the interaction of the  $\sigma^*$  and  $\pi^*$  orbitals was found for some  $\alpha$ -haloketones [29] and was postulated [5] in order to explain the differences in the primary processes of photolysis of  $\alpha$ -haloesters, as compared with  $\beta$ - and  $\gamma$ -derivatives. In spite of this, some authors point rather to the possibility of an intramolecular energy transfer from the excited state of the phenyl group to the carboxyl group, as an alternative to delocalized excitation of the whole molecule [26]. In order to get some additional information as to whether or not the C-Cl bond homolysis in I can be connected with the absorption of radiation by the benzene ring, and next with intramolecular energy transfer to the  $HC(Cl)COOEt$  group, investigations were performed on intermolecular energy transfer from the benzene molecule to  $ClCH_2COOEt$ . The photolysis of equimolar mixtures of both these compounds in cyclohexane at  $\lambda \approx 254$  nm has shown that the energy transfer takes place and that the  $\Phi$  value of the appearance of HCl, the main product of direct photolysis of  $ClCH_2COOEt$ , is equal to  $0.41 \pm 0.06$ . Thus, it can be seen that

the data obtained do not give an unequivocal answer to the mechanism leading to the C-Cl bond homolysis in I. The current investigations on the effect of relative positions of the phenyl, carboxyl, and C-Cl groups on photochemical properties of the esters, derivatives of  $\beta$ -phenylpropionic acid, should largely contribute to a better understanding of the mechanism of excitation and photolysis of these and other aromatic haloesters.

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