

PHOTOLYSIS OF SOME DICHLOROACETIC ACID ESTERS IN CYCLOHEXANE

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Summary

Quantitative analysis has been performed on the products of direct as well as benzene- and acetone-sensitized photolysis of ethyl and methyl dichloroacetates in cyclohexane. Their quantum yields have been determined. It has been found that the primary mechanism is similar to that for corresponding α -monochloroacetic acid esters and consists mainly in homolytic cleavage of the C-Cl bond. The short-lived excited state of these esters, most likely the singlet state, is responsible for this reaction. The lack of fluorescence and the efficiency of the C-Cl rupture approaching unity, indicates that other decay processes for these esters does not play a considerable role. The maximum lifetime of the excited singlet state for these ester molecules is $\tau_s < 2 \times 10^{-11}$ s. Photolysis of dichloroacetic acid esters can be sensitized by benzene and acetone. In the case of benzene the energy transfer occurs from the excited singlet of the donor, and both the classical energy transfer, [singlet(benzene) \rightarrow singlet(ester)], and the formation of an exciplex between the excited donor molecule and the acceptor molecule in the ground state, are possible.

Introduction

Studies on the photochemical mechanism of a series of A, A'-substituents in the vicinity of carboxyl group of the esters, $\overset{\text{O}}{\parallel}\text{COA}'$, have been extended

in this paper to dichloroacetic acid derivatives, where A = $-\text{CHCl}_2$, A' = CH_3 (Me) (I) or C_2H_5 (Et) (II). Our earlier studies were concerned with a series of α -monohalogenesters, derivatives of formic acid and acetic acid [1 - 3], and with aromatic esters, derivatives of α - and β -naphthylacetic and phenylacetic acids [4, 5]. It was found that the C-X bond homolysis (X = halogen atom) is the main primary process of photolysis of the first group of the above-mentioned compounds. In contrast to α -monohalogen esters, reactions of homolysis of the C-X bond play no important part in the photo-

lysis of β - and γ -monohalogenesters [6] for which, the type II reactions and decarboxylation reactions, are the principal photochemical pathways.

The aim of the present work is to determine the effect of a second α -halogen atom on the mechanism of photolysis of chloroacetic acid esters in cyclohexane. In order to determine the competition role the type II reactions in the photochemistry of these compounds, methyl (I) and ethyl (II) dichloroacetate were investigated.

Experimental

Esters I and II (Fluka, 99.8% puriss.) were dried over anhydrous MgSO_4 and distilled under reduced pressure immediately before use.

Acetone (Merck, spectrally pure) and dimethyl α, α' -dichlorosuccinate (III) (Schuchardt) were used without additional purification. The remaining reagents (analytically pure) were dried before use and distilled.

A TQ-150 high-pressure and a TNN-15/32 low-pressure mercury-vapour lamps (both of Original-Hanau) were used, emitting practically monochromatic 254 nm radiation. Irradiations were performed in "merry-go-round" (MGR) system [3]. Preparative photolyses were run as previously described [7].

Uranyl oxalate actinometry was employed. Quantitative absorption data for each of the esters are given in the Tables. Quantitative and qualitative determinations of the photolysis products were made by vapour phase chromatography (v.p.c.) as well as by i.r., u.v., and mass spectrometry. In the case of liquid products such as $\text{ClCH}_2\text{COOMe}(\text{Et})$, $\text{C}_6\text{H}_{11}\text{Cl}$, $(\text{C}_6\text{H}_{11})_2$ and the majority of volatile products, qualitative analysis consisted of the comparison of retention times of standards with the reaction products, using a variety of v.p.c. columns. This method was also used to determine the presence of ester III. Carbon monoxide and carbon dioxide were determined by the method described previously [7].

For $\text{C}_6\text{H}_{11}\text{CH}(\text{Cl})\text{COOMe}(\text{Et})$ (IV and V) the respective products were isolated by preparative gas chromatography and analyzed by mass and i.r. spectrometry. For ester IV, for example, the following data were obtained: mass spectrum (m/e , %): 59(5.7), 83(8.3), 108(100.0), 110 (32.1), 155 (1.2), 190 (0.18), 191 (0.06), 192 (0.06); i.r. (CS_2 , cm^{-1}): 2982 w, 2920, 2843, 1745, 1745 s, 1415, 1360 w, 1340 m, 1322 w, 1287 m, 1262 s, 1233, 1213 w, 1185 m, 1152 s, 1123 w, 1015, 995 m, 953, 922, 897, 885, 872, 850, 840, 735, 720, 705 w.

Quantitative v.p.c. analysis was performed on 7 or 9 ft. columns of Triton X-305 on Chromosorb W (80 - 100 mesh) employing the following temperature programme: 50 °C for 8 min; 8 °C/min, 150 °C for 20 min; or OV-17 on the same support, temperature programme: 90 °C for 4 min; 17 °C/min; 240 °C for 25 min. For the volatile products, Porapak Q (100 - 120 mesh) was used with the following temperature programme: 100 °C for 5 min; 40 °C/min; 200 °C for 30 min. Nitrogen was the carrier gas (flow rate, 3 l/h). These measurements were performed on a Pye 104 gas chromatograph

equipped with flame ionization detector, employing cyclooctane and cyclo-decane as internal standards.

Ester IV was isolated preparatively on a Hewlett-Packard 5750 gas chromatograph with thermal conductivity detector, using a 7 ft. UCW-98 on Chromosorb W (80 - 100 mesh) columns at programmed temperature: 100 °C for 8 min; 10 °C/min; 270 °C for 10 min and with helium carrier gas at a flow rate of 2 l/h.

The following spectrophotometers were used: for i.r. measurements, Acculab 3 (Backmann) and UR-20 (Zeiss); for u.v. measurements, SP-700 (Unicam), VSU-2 (Zeiss) and Specord (Zeiss), and also a Varian MAT CH5 mass spectrometer.

HCl was determined by potentiometric titrations according to the method described previously [8].

Fluorescence measurements for esters I and II were carried out on a Perkin-Elmer MPF-3 spectrofluorimeter both in cyclohexane and n-pentane in 1 cm quartz cells. Concentrations of esters corresponding to absorptivities from 0.01 to 2.0, different $\lambda_{exc.}$, maximum sensitivity and optimum slits of the instrument were employed. The least square method was used to calculate the slope of the Stern-Volmer equations for quenching of benzene ($9.1 \times 10^{-3} M$) fluorescence.

In the case of photolysis of acetone-sensitized esters the number of radiation quanta absorbed by acetone was determined as follows: polychromatic radiation emitted by the high-pressure mercury-vapour lamp was passed through a Pyrex filter and then through a filter solution of acetone in cyclohexane of the same concentration and depth as that used in the photolysis. The number of quanta absorbed by acetone in the photolysis solution was determined from the difference in the intensity of radiations passing through the acetone+cyclohexane filter and the total radiation intensity emitted by the lamp.

Results

Absorption spectra of esters I and II in cyclohexane

It can be seen from Table 1 that the introduction into the ethyl acetate molecule of successive α -chlorine considerably affects the position and intensity of the long wavelength absorption band of the ester.

A considerable broadening and bathochromic shift of the absorption bands are observed, as well as the increase in their intensity, the effect increasing as the number of Cl atoms in the molecule increases. The intensities ($\alpha = 81 - 162$) and the hypsochromic shifts of the absorption bands in polar solvents (methanol) are characteristic of the n, π^* type transition of the ester carbonyl group. The broadening and bathochromic shift of the absorption band with chlorine substitution show that there are energy differences for n, π^* transition for unsubstituted and Cl-substituted esters which can be ascribed to inductive and resonance effects from Cl atoms. A similar, though

TABLE 1

Molar absorptivities, a , and absorption maxima λ_{\max} , of some α -halogenoacid esters

Ester	In cyclohexane			In methanol
	λ_{\max} (nm)	a_{\max} ($M^{-1} \text{ cm}^{-1}$)	a_{254}	λ_{\max} (nm)
$\text{Cl}_2\text{CHCOOMe}$	224	153	17	217
$\text{Cl}_2\text{CHCOOEt}$	225	162	24	218
$\text{ClCH}_2\text{COOEt}$	217	81	7	208
CH_3COOEt	211	58	0	204 ^a

^aIn H_2O [10].

slight, effect is also observed when the length of the alkyl chain (A) joined

to the carboxyl group in $\text{A}-\overset{\text{O}}{\parallel}{\text{C}}\text{OA}'$ is increased [9, 10].

Analysis of products and quantum yields of the photolysis of esters I and II in cyclohexane

The analysis of products of photolysis of esters I and II in cyclohexane showed the presence of the following compounds:

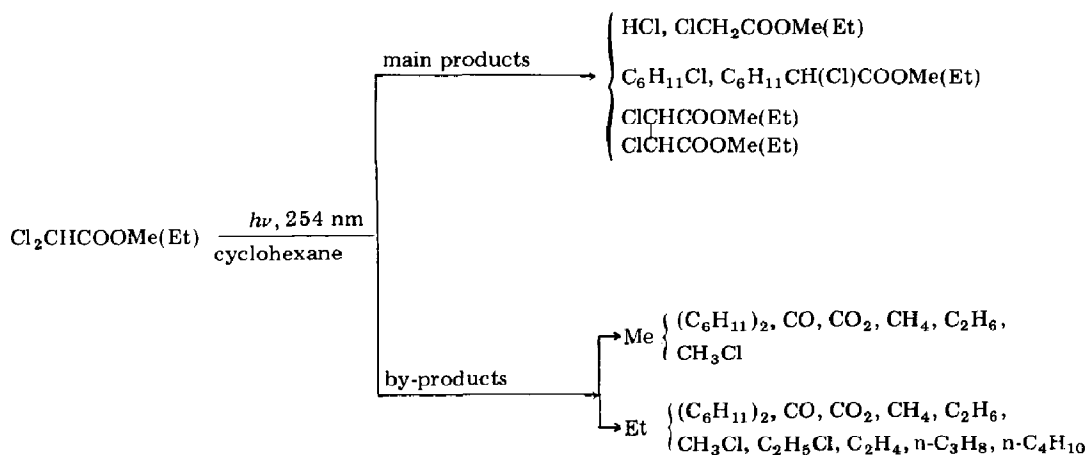


Table 2 gives the quantum yields, Φ , for the disappearance of esters I and II, and for the formation of the main photolysis products. In this case data from conversions of up to 25% were extrapolated to 0% conversion. For comparison, Table 2 also gives analogous Φ values for ethyl α -monochloroacetate, determined earlier [2].

Trace amounts of gases formed during photolysis were determined semi-quantitatively by comparison with methane as an internal standard for a given ester. In addition, relative quantum yields of the formation of more important gaseous products were determined, assuming the Φ values

TABLE 2

Quantum yields of main products of methyl and ethyl α, α -dichloroacetates photolysis in cyclohexane at $\lambda \approx 254 \text{ nm}^a$.

Photolysis product	$\text{Cl}_2\text{CHCOOMe}$ (I)	$\text{Cl}_2\text{CHCOOEt}$ (II)	$\text{ClCH}_2\text{COOEt}^b$ (VI)
ester disappearance	1.0 \pm 0.2	1.0 \pm 0.2	1.0 \pm 0.2
HCl ^c	0.74 \pm 0.08 ^e 0.74 \pm 0.08 ^f	0.76 \pm 0.08 ^e 0.76 \pm 0.08 ^f	0.67 \pm 0.06 ^e 0.67 \pm 0.06 ^f
$\text{ClCH}_2\text{COOMe}(\text{Et})$	0.33 \pm 0.05	0.38 \pm 0.05	—
CH_3COOEt	—	—	0.4 \pm 0.1
$\text{C}_6\text{H}_{11}\text{Cl}$	0.22 \pm 0.05	0.20 \pm 0.05	0.14 \pm 0.05
$\text{C}_6\text{H}_{11}\text{CH}(\text{Cl})\text{COOMe}(\text{Et})$	0.19 \pm 0.05	0.14 \pm 0.05	—
$\text{C}_6\text{H}_{11}(\text{CH}_2)\text{COOEt}$	—	—	0.20 \pm 0.07
$\text{ClCHCOOMe}(\text{Et})$	0.07 \pm 0.02	0.07 \pm 0.02	—
$\text{ClCHCOOMe}(\text{Et})$ (C_6H_{11}) ₂	0.04 \pm 0.01	0.03 \pm 0.01	d

^aQuantum yields were determined by extrapolating the results of several runs to 0% conversion, mean light input, L.I. = $(4.3 \pm 0.3) \times 10^{-2} \text{ mE h}^{-1} \text{ cm}^{-3}$.

^bThese values were taken partly from ref. [2].

^cLight input, L.I. = $(2.7 \pm 0.3) \times 10^{-2} \text{ mE h}^{-1} \text{ cm}^{-3}$.

^dNot measured.

^eSamples after deaeration by nitrogen [21].

^fSamples saturated by air before irradiation.

of the respective products for $\text{ClCH}_2\text{COOEt}$ as equal to unity. This semi-quantitative analysis makes it possible to estimate the formation of gas products of photolysis in various systems, and to determine the relative participation of other primary processes in the photolysis.

Fluorescence of esters I and II

No measurable fluorescence was observed for these esters. Comparative studies using acetone as fluorescence standard have shown that limiting value for fluorescence quantum yields of the order of 1×10^{-5} can be detected. Thus, it can be assumed that the investigated esters do not fluoresce with quantum yields greater than the value given above.

Approximate estimation of the lifetime of the excited state E^* responsible for C-Cl bond homolysis and of the singlet lifetime

From the negative oxygen effect on the Φ_{HCl} values (Table 2) one can roughly estimate, using the simple Stern-Volmer relationship, the lifetime, τ_{max} , of the excited state E^* . Because the rate constants of oxygen quenching of esters singlet and triplet states are not available and might be different [11] we used here the value $K_q[\text{Q}] = 6 \times 10^7 \text{ s}^{-1}$ obtained from fluorescence quenching measurements [12], where K_q is close to the diffusion controlled reaction. Thus, the estimated lifetime of the excited state E^* for both esters

TABLE 3

Ratios of v.p.c. peak heights^a, i.r. absorption bands heights and relative quantum yields Φ^b for some gaseous products formed during $\text{Cl}_2\text{CHCOOMe}(\text{Et})$ photolysis in cyclohexane at $\lambda \approx 254 \text{ nm}^c$.

Ester	CH_4^a	C_2H_4	C_2H_6	Φ^b		Φ^b		
				$\frac{\text{C}_2\text{H}_4}{\text{C}_2\text{H}_6}$	CO^d	CH_4	C_2H_4	C_2H_6
$\text{Cl}_2\text{CHCOOMe}$ (I)	1	0	~ 0.006	0	1.2	4.5	0	~ 0.03
$\text{Cl}_2\text{CHCOOEt}$ (II)	1	0.38	9.1	0.04	1.1	0.8	1.5	8.0
$\text{ClCH}_2\text{COOEt}$ (VI)	1	0.20	0.9	0.2	2.8	1	1	1

^aMethane peak height for each ester is taken as equal to unity.

^b Φ values for $\text{ClCH}_2\text{COOEt}$ are taken as equal to unity.

^cLight input, L.I. = $(2.7 \pm 0.3) \times 10^{-2} \text{ mE h}^{-1} \text{ cm}^{-2}$, determined after 5 h of irradiation, modified method, described earlier [22] was used.

^dThe ratio of heights in mm of the respective i.r. absorption bands, $\text{CO}(2100 - 2200 \text{ cm}^{-1})$, $\text{CO}_2(2300 - 2400 \text{ cm}^{-1})$, 10 cm gas cell with sodium chloride windows and constant pressure $5 \times 10^{-2} \text{ mmHg}$ was used.

is approximately equal to $\tau_{\text{max}} < 2.2 \times 10^{-9} \text{ s}$. This indicates that the C-Cl bond homolysis probably proceeds from the singlet state or from a very short-lived triplet.

On the other hand, the lifetime of the singlet state, τ_s can be estimated approximately, from the relationship $\tau_s = \Phi_f k_f^{-1}$, where k_f is the fluorescence rate constant from S_1 which, can be evaluated from the integration of u.v. absorption band [13]. The estimated k_f values are: 5.9×10^6 and $6.5 \times 10^6 \text{ s}^{-1}$ for esters I and II, respectively. Now, assuming for both esters the values $\Phi_f < 1 \times 10^{-5}$ maximum values can be estimated for the lifetime of the singlet state, $\tau_{s(\text{max})} < 2 \times 10^{-12} \text{ s}$.

Photolysis of esters I and II sensitized by benzene and acetone

In order to obtain additional information concerning the energy and type of excited states for these esters, preliminary mechanistic investigations were performed with selected sensitizers and quenchers. In the case of halogen acid esters such studies are difficult to perform because: (i) lack of appropriate sensitizers of singlet state energy $E_S > 110 \text{ kcal/mol}$ or of triplet state energy $E_T > 85 \text{ kcal/mol}$. It is estimated that in the case of simple, unsubstituted esters and acids the E_S value is of the order of 109 - 114 kcal/mol [14 - 16]. Assuming a singlet-triplet energy splitting of the same order as in ketones (6 - 8 kcal/mol), the E_T values for the esters can be estimated to be of the order of 101 - 108 kcal/mol [14 - 16]; (ii) limitations on the use of commonly applied triplet state quenchers with $E_T < 80 \text{ kcal/mol}$. These limitations result from the necessity of using exciting wavelengths of $\lambda \approx 254 \text{ nm}$, the same spectral region that most quenchers have appreciable

TABLE 4

Quantum yields of HCl formation during sensitized by benzene and acetone photolysis of esters of dichloroacetates in cyclohexane.

Ester	Direct photolysis	Benzene ^a	Acetone ^b
Cl ₂ CHCOOMe	0.74 ± 0.08	0.45 ± 0.04	0.14 ± 0.04
Cl ₂ CHCOOEt	0.75 ± 0.08	0.45 ± 0.04	0.15 ± 0.04

^a~95% radiation absorbed by benzene, $\lambda \approx 254$ nm, extrapolated to 0% conversion of ester.

^bAcetone concentration 0.5 M; ester concentration dependent, values at 0.1 M concentration of ester, $\lambda \approx 300 - 320$ nm.

molar absorptivities, α . This prevents the use of very high concentrations of quenchers for trapping of very short-lived states. Additionally, studies of this kind are complicated by the possible radical reactions with the quenchers [36].

Benzene sensitization ($E_s = 110$ kcal/mol [17]) of the photolysis of esters I and II was investigated at $\lambda \approx 254$ nm, where benzene absorption is relatively large. Because of the appreciable absorption of the esters in the spectral region of absorption of sensitizer (benzene), quantum yield measurements were performed in this case with constant concentration of benzene and of the esters, adjusted in such a way that ~95% of radiation at $\lambda \approx 254$ nm was absorbed by benzene. The progress of reaction was followed by quantum yield measurements of HCl, the major product of photolysis of esters I and II. Benzene was found to sensitize the photolysis of esters I and II (Table 4).

In order to find whether the benzene singlet state takes part in the energy transfer process, quenching of benzene fluorescence in the presence of esters I and II was investigated. Both esters were found to quench benzene fluorescence efficiently. The absorption spectrum of benzene in cyclohexane did not change as a result of addition of esters I and II. The unquenched portion of benzene fluorescence had the same spectral distribution as that in solutions without quenchers. No new fluorescence bands were observed. Linear Stern-Volmer plots were obtained; quenching rate constants, k_q , derived from these plots, are given in Table 5.

Moreover, it has been found that photolysis of esters I and II can be sensitized by acetone even though the singlet state energy ($E_g = 88$ kcal/mol) and the triplet state energy ($E_T = 79 - 82$ kcal/mol [17]) of acetone are probably much lower than those of the esters. Therefore, the classical exothermic energy transfer is improbable in this system. The course of photosensitized reaction was observed by quantum yield measurements of the major products (HCl). The lack of absorption of esters I and II within the acetone absorption range allowed the investigation of the effect of ester concentration, $C_{I,II}$ on Φ_{HCl} at constant, low acetone concentration (0.5 M) which still ensured complete absorption of the incident radiation by acetone

TABLE 5

Rate constants (k_q) of quenching of benzene fluorescence by esters I and II in cyclohexane.

Ester	$(k_q \tau_d)^a [M^{-1}]$	$k_q [M^{-1} s^{-1}]$	$\tau_d^b [ns]$
$Cl_2CHCOOMe$	31.4	2.6×10^9	12.2
$Cl_2CHCOOEt$	13.6	1.1×10^9	12.2

^aCalculated using least squares method, after taking into account the competitive absorption of esters at 254 nm.

^bThe lifetime of excited singlet state of benzene in aerated cyclohexane [23].

[18, 19]. Φ_{HCl} increased with the increase in the concentration of I and II within the range 0.001 - 0.1 M, had almost constant value within the concentration range 0.1 - 3 M, and slightly decreased at higher concentrations of esters. This slight decrease of Φ_{HCl} may be due to the increased probability of recombination reaction of the radicals in the solvent "cage" which is probably connected with a considerable decrease in the cyclohexane concentration in the system. No effect of deaeration of the system on Φ_{HCl} has been observed. Maximum Φ_{HCl} values for esters I and II are collected in Table 4. Making use of the linear dependence of Φ_{HCl}^{-1} on the reciprocal esters concentration $C_{I,II}^{-1} (M^{-1})$ within the concentration range 0.001 - 0.1 M, it is possible to calculate sensitization constants, K_s , from the intercept to slope ratio applying the kinetic analysis devised previously for such systems [18, 20] and assuming that energy transfer proceeds from the acetone singlet state:

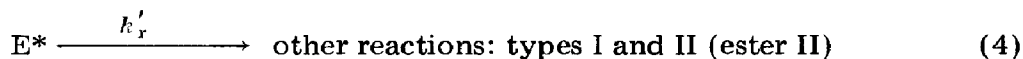
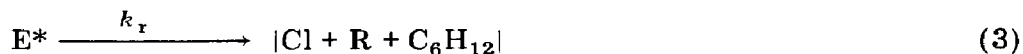
$$K_s = k_s \tau_a$$

where k_s is the energy transfer constant from acetone singlet to the ester molecule, and τ_a is the lifetime of the singlet state of the donor (*i.e.*, acetone).

Thus, established values of sensitization constants are, respectively, 35 and 30 M^{-1} for esters I and II, and the calculated k_s values are equal to 8×10^9 and $7 \times 10^9 M^{-1} s^{-1}$, assuming the value $4.4 \times 10^{-9} s$ [19] as τ_a .

Discussion

The experimental data allow us to suggest the following mechanism for the photolysis of dichloroacetate esters (in the scheme, E denotes $Cl_2CHCOOMe$ (Et)):

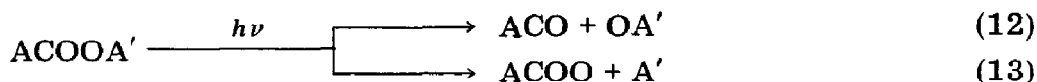


of the products in reactions (6a) and (7a) seems to be more probable than in reactions proceeding outside the "cage", *i.e.* reactions (6b) and (7b). However, the role of reaction (8) in the formation of the main photolysis products cannot be excluded. The appearance of relatively large amounts of $(C_6H_{11})_2$ and R_2 in reactions (9) and (10) shows that at least some part of radicals C_6H_{11} and R can become kinetically "free" and escape the "cage" either in reactions (6b) and (7b) or in reaction (8). Because of the complexity and a great variety of possible radical reactions proceeding in this system (scheme), the quantitative determination of the role of the "cage" effect in the formation of the main photolysis products (reactions 6 and 6a, 7 and 7a) in comparison with the formation of these products outside the "cage" (reactions 6b, 7b and 8a, 8b) is very difficult.

The comparison of the quantum yields of ester disappearance (Φ_{dis}) with the sum of the values of quantum yields of the formation of Cl (Φ_{Cl}) and R-containing (Φ_R) products are of interest. In particular, for the esters the three values are, respectively: 1.0 ± 0.2 , 0.96 ± 0.13 , 0.66 ± 0.14 . From this comparison it can be seen that Cl formed in reaction (3) is found in products of the type $C_6H_{11}Cl$ and HCl, whereas the radical R formed in the same reaction is found mainly in the products of RH, $C_6H_{11}R$ and R_2 type. The remaining radicals R which are not accounted by these products, could react with starting ester, with the solvent, or with other radicals formed in the reaction (*e.g.* from photolysis of α -monohalogenesters of RH and $C_6H_{11}R$ type) generating high-boiling compounds (trace amounts were observed on chromatograms at high ester conversion). Also, some part of the R radicals can decompose, resulting in a number of the observed gas products. The analysis of these products indicates that the type I and II reactions do not play a significant role in the photolysis of esters I and II ($\Phi_{Cl} \approx 1$). During the photolysis of ester II small amounts of C_2H_4 were formed indicating that the primary type II process is occurring, although it accounts for only a limited portion of the products as in the case of α -monohalogen-substituted ester VI (Table 3). However, it is difficult to say if these small quantities of C_2H_4 are formed in a primary process, or as a result of secondary processes connected with disproportionation of C_2H_5 radicals which are present in the photolysis of esters II and VI as confirmed by the production of ethane (Table 3). The ratio of the rate constant k for C_2H_5 radicals disproportionation to the rate constant for their recombination in iso-octane, k_c , is $k/k_c = 0.16$ at $25^\circ C$ [27]. The presence of n-butane in the products of photolysis II is further evidence that at least some part of C_2H_4 can be formed from disproportionation of C_2H_5 radicals.

From the data in Table 3 it can be seen that the hydrogen abstraction reaction by Me and Et radicals for esters I and II proceeds much more rapidly than recombination reactions as determined by the relatively large CH_4 to C_2H_6 production for ester I, and also from the relative $C_2H_6/n-C_4H_{10}$ production for ester II. Large quantum yields of CH_4 and C_2H_6 for esters I and II, respectively, when compared with VI, point to the larger role of the type I reaction in the case of dichlorosubstituted esters in comparison with α -monochlorosubstituted ester. The increase of the CO/CO_2 value for ester VI

in comparison with esters I and II suggests that for dichloroesters the relative role of reactions (12) and (13):



is smaller than for α -monochlorosubstituted esters. Some of the volatile products can also form, as a result of decomposition of the R radicals (*vide supra*), thus making it difficult to determine the quantitative role of reaction (4) in the process of deactivation of E^* .

From the comparison of data in Table 2 which shows that analogous products are formed from the photolysis of acetic acid α , α -dichloro-, and α -monochloro-derivatives, a general reaction mechanism can be suggested for the chlorinated esters and that C-Cl homolysis is the main primary process.

Chemical determination by sensitization of the nature of ester excited states (E^*), responsible for the C-Cl homolysis meets with considerable experimental difficulty. However, an estimation can be made for the lifetime of state E^* of $\tau < 2.2 \times 10^{-9}$ s and $\tau_s < 2 \times 10^{-12}$ s for the singlet. The Φ_{Cl} values, approximately equal to one, and the short lifetime of the excited state shows that the rate constants of esters dissociation in excited state must be very high. Dissociation rate constants from excited singlet states for aryl esters were evaluated to be of the order 10^{12} - 10^{14} s $^{-1}$ [34, 35].

From benzene- and acetone-sensitized photolysis of esters I and II the identity of E^* could not be unequivocally assigned. In both cases the transfer of energy takes place, which was not observed in the case of benzene-simple aliphatic acids systems [28]. The transfer of energy from benzene singlet state to the esters is responsible for their photochemical transformation which is confirmed by: (i) effective quenching of benzene fluorescence in the presence of esters I and II (Table 5); (ii) a high Φ_{HCl} value (0.45) as compared with quantum yield of intersystem crossing $\Phi_{S_1 \rightarrow T_1}$ in benzene (0.25) [30, 31]*. Both classical energy transfer of the type singlet (benzene) \rightarrow singlet (ester)** and through the formation of an excited complex (exciplex) between the excited singlet benzene or acetone and the ester in the ground state seems to be probable. Such complexes have been postulated for the fluorescence quenching of a number of other aromatic compounds, with $\text{ClCH}_2\text{COOMe}$ [32, 33], and in the case of acetone-sensitized photolysis of 1,4-dichlorobutane [18, 19].

However, much more data are needed to ascertain the mechanism of the benzene/ester and acetone/ester interactions, and detailed discussion will await the results of the experiments which are now in progress.

*The $\Phi_{S_1 \rightarrow T_1}$ value depends on the benzene concentration and is equal to 0.56, 0.47 and 0.23, respectively, at benzene concentrations in cyclohexane of 11.2, 5.1 and 0.11 M [29]. For the benzene concentration in cyclohexane used in this work (~ 0.33 M) one can assume a value of ~ 0.25 , which has been estimated independently [30, 31].

** Approximate locations of the 0-0 bands of esters I and II estimated from its absorption spectra by the method of Lewis and Kasha [37] are 264 nm which correspond to singlet energies of 108 and 107 kcal/mol, respectively.

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