of those estimated for the hydroxymercuration of olefinic compounds by other organomercurial ions from measurements on the rates of exchange of olefins with oxymercurials.[9] Also pertinent to the present theme are recent direct observations of the acid-induced cleavage of diacetonylmercury[10] and of the methoxymercuration of an allene by organomercury(II) ions.[11]

Finally, the results of these studies yield information, not previously available, about the effects of the systematic variation of R in the series of RHg^+ ions examined, both on the equilibrium constant (K_3) of the oxymercuration reaction 3 and on the rate constant (k_4) of the acid-promoted deoxymercuration reaction 4. The data in Table I reveal a marked parallel between the variations of the two constants, each of which appears to exhibit an inverse dependence on the electron donor strength of R. These trends are reflected in the Hammett plots for the $X–C_6H_4Hg^+$ ions in Figure 6 which yield ρ values of approximately 0.5 for k_4 and 0.6 for K_3. The direction of the trend for K_3 is readily understood in terms of the influence of increasing electron donation from the R substituent in RHg^+ which is expected to lower the effective positive charge (*i.e.*, electrophilic character) of the Hg atom and, correspondingly, its tendency to form a second mercury–carbon σ bond (*i.e.*, to coordinate a second R^- substituent). The origin and significance of the corresponding trends for k_4, which are expected to be influenced by several compensating factors, are less obvious.

Acknowledgments. Support of this work through grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Photolysis of Phenylacetic Acid and Methyl Phenylacetate in Methanol[1]

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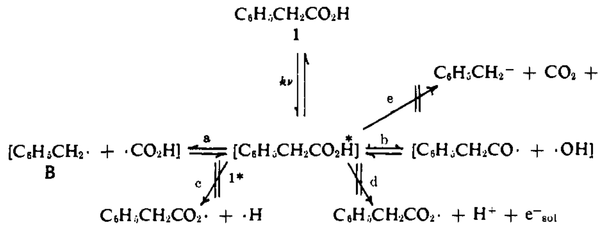
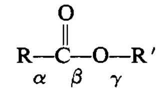
Abstract: Detailed decomposition mechanisms of phenylacetic acid (**1**) or its methyl ester (**2**) on photolysis are outlined. The photoproducts (Φ) in methanol of **1** at 26° are CO_2 (0.037), CO (0.013), $(C_6H_5CH_2)_2$ (0.029), $C_6H_5CH_2CH_2OH$ (0.005), $C_6H_5CH_3$ (0.002), and of **2** at 31° are CO_2 (0.02), CO (0.028), CH_4 (0.009), $(C_6H_5CH_2)_2$ (0.02), $C_6H_5CH_2CH_2OH$ (0.01). Both **1** and **2** also yielded substantial quantities of polymer. Following excitation (280–210 nm), the primary processes involve cleavage of the carboxyl function at two bonds: in **1**, either benzyl (B) and carboxyl (CO_2H) or phenylacetyl and hydroxyl radicals are formed; in **2**, analogous transient pairs are formed. Benzyl radicals recombine to form bibenzyl, react with hydroxymethyl radicals, and may add to the growing acidic polymer. The hydroxyl and methoxyl radicals probably abstract hydrogen from methanol, while the carboxyl species (CO_2H or CO_2CH_3) react with methanol to give formic acid or ester. Reactions that may be ascribed to the solvated electron and hydrogen atoms appear to be insignificant, although the trace of toluene produced from **1** probably arises from the benzyl anion. A general scheme covering the cleavage modes of the carboxyl function *via* homolytic and heterolytic processes is outlined.

Grossweiner and Joschek have surveyed a large number of aromatic molecules for the formation of the solvated electron by flash photolysis.[2] Subsequently, detailed mechanisms and product patterns were developed for the photochemical behavior of phenols and related derivatives.[3] Here, we are concerned with the several routes by which irradiated phenylacetic acid (**1**) and methyl phenylacetate (**2**) go to their products.[4] Although **1** might be regarded as the parent of some acids and a model for others, it turns out that this view could be misleading with respect to the photobehavior of carboxylic acid derivatives in general.[5]



(1)

Most simple acids and esters absorb light below 280 nm (>102 kcal/mol), so that enough energy is available to break any of the bonds indicated[5a]



$$\underset{\alpha}{R}\overset{O}{\underset{\beta}{\overset{\|}{—C—}}}\underset{\gamma}{O—R'}$$

3

For simple compounds, *e.g.*, formic acid, acetic acid, methyl formate, and methyl acetate, β photocleavage predominates; there is substantial γ cleavage in acetic acid and a number of other minor paths are generally

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(1) Taken from the Ph.D. Thesis of T. O. M., Illinois Institute of Technology, 1970. Financial support from the Federal Water Pollution Control Administration in the form of a fellowship for T. O. M. and from Public Health Service Grant GM 7021 is gratefully acknowledged.

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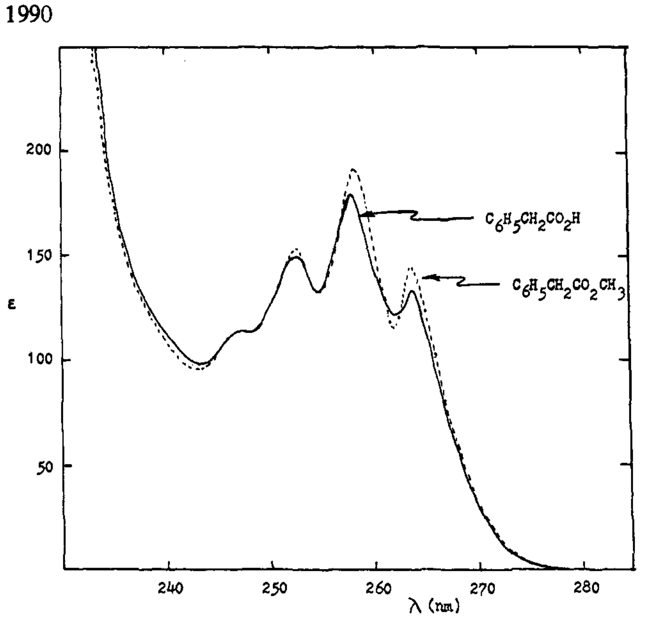

Figure 1. Ultraviolet absorption spectrum of phenylacetic acid and methyl phenylacetate in methanol.

present. In the photolyses of molecules "related" to **1**, the major path, usually among many, has taken phenylacetic acid to benzyl (in a matrix),[6a] 1-naphthylacetic acid to naphthalene and 1-methylnaphthalene,[6b] phenylalanine to tyrosine,[6c] chlorophenylacetic and 2,3,6-trichlorophenylacetic (FENAC) acids to dechlorinated materials,[6d] (2-pyridyl)acetic acid to 2-picoline,[6e] mandelic acid (with added azo dye) to benzaldehyde,[6f] sodium phenylglycidate to phenylacetaldehyde and bibenzyl,[6g] some nitrophenylacetates to corresponding toluenes,[7] and other nitrophenylacetates to corresponding bibenzyls.[7] The transients observed in the flash photolyses of the anions of arylalkyl acids in water are interesting: the solvated electron was obtained from benzoate, phenylacetate, β-phenylpropionate, γ-phenylbutyrate, and δ-phenylvalerate in water; radical spectra were not observed for the last three anions, but B from **1** and possibly $C_6H_6COO\cdot^-$ from benzoate were noted.[2] Evidently, there is a fair amount of individual photochemical behavior among carboxylic acids.

In this work, we attempt to sort out those reaction routes which are specific to the title compounds and those which apply to the photolysis of carboxylic compounds in general.

Experimental Section

Melting points, determined with a Mel-Temp (block) apparatus, and boiling points are uncorrected. Nmr spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Infrared (ir) spectra were obtained on a Perkin-Elmer Model 257 grating spectrometer. Ultraviolet absorption (uv) spectra were determined on a Beckman DK-2A spectrophotometer.

Materials. Baker absolute methanol was used for the steady-state irradiations, but was purified for spectral work by refluxing for 2 hr in the presence of 2,4-dinitrophenylhydrazine and sulfuric acid, followed by distillation under nitrogen, ϵ(250 nm) <0.02. Reagent grade 2-propanol, spectrograde cyclohexane, and triply distilled water were used as solvents. After decolorizing with carbon, phenylacetic acid (**1**) was recrystallized from petroleum ether, mp 75.5–76.5° (lit.[8] mp 77°), >99.7% pure by titration. Methyl phenylacetate (**2**) was prepared from **1** in absolute methanol, bp 78° (1 mm), n^{35}D 1.5022 (lit.[9] bp 83–85° (6 mm), $n^{25.5}$D 1.5051). Gas phase chromatography (gpc) indicated no extraneous peaks in **2**; hydrolysis followed by back titration with standard acid showed this ester to be >98.5% pure.

Steady-State Irradiations. Our flash photolysis apparatus will be described elsewhere.[4] Steady-state irradiations were carried out in a Pyrex vessel containing a removable double-jacketed quartz immersion well. The vessel contained up to 700 ml of solution which was mixed by bubbling gas through a fine frit at the bottom; the purge gas also swept gaseous photoproducts out of an exit port at the top of the vessel. A rubber septum was located on another port so that aliquots could be removed by syringe. A thermometer was immersed in the solution through a ground joint in the side of the vessel. The temperature was regulated to *ca.* ±2°, by controlling the flow of cooling water passing through the quartz immersion well. A medium-pressure mercury lamp (Hanovia Type L 679A, 450 W, 135 V, 3.6 A, and 4.5 in. arc) was used as the light source. Wavelengths both above and below 254 nm are put out by this lamp, but those below 210 nm were effectively removed by a sleeve of Vycor 7910 glass.

The photohydrolysis of aqueous chloroacetic acid was used as an actinometer.[10] Since 1 *M* chloroacetic acid absorbs strongly only below 280 nm, the light intensity measurements were effectively confined to the region between 280 and 210 nm. Quantum yields (Φ) for the production of hydrochloric acid were only measured at the 2537-Å mercury resonance emission and are temperature dependent.[10] Nevertheless, these values should be a good estimate for the average Φ. Presumably all of the light was absorbed, since plots of acid formed vs. time gave the expected zero-order dependence. At 25°, the lamp intensity was found to be 1.21×10^{19} quanta/sec for $\Phi = 0.31$. Three determinations over a 1-year period varied <4%. Because the lamp was completely immersed during an irradiation, all of the light was absorbed and no geometry corrections were required. Since all of the materials irradiated in this study absorbed similarly in the general region of 210–280 nm (Figure 1), differences in total light absorption were considered negligible and the same initial values were used in all cases.

Wet Analyses. Standard methanolic base was used to monitor the phenylacetic acid. A Corning Model 10 pH meter was used to measure the equivalence point. In order to avoid precipitation of water-insoluble compounds, but still have sufficient water to use a combination glass electrode, 10 ml of 50% aqueous methanol was added to the aliquots prior to titration. Carbon dioxide (from irradiation studies) was absorbed in standard sodium hydroxide solution. The carbonate was then precipitated with barium chloride and the loss as barium carbonate was determined by titrating the remaining base with standard hydrochloric acid. The yields of carbon dioxide obtained by this procedure were always *ca.* 5–10% lower than those obtained by gpc. Tests showed that at least 3% of the carbon dioxide was lost by inefficient trapping by the sodium hydroxide, even at low flow rates.

Chloride ion was determined potentiometrically with standard silver nitrate (0.0263 *M*).

Methyl phenylacetate was analyzed titrimetrically. In a typical experiment, 1-ml aliquots were placed in 15-ml vials equipped with screw caps lined with plastic. The methanol was evaporated on a water bath to remove any dissolved carbon dioxide. A slight excess of base in 50% aqueous methanol was added to each vial. The capped vials were heated 1–2 hr on a steam bath to promote hydrolysis, then cooled, and titrated to a phenophthalein end point with standard acid. The decrease in base concentration due to hydrolysis determined the ester concentration. Reproducibility was better than 2%.

In the absence of interferences, the amount of bibenzyl (BB) or toluene in a cyclohexane extract could be determined by comparing the uv absorption spectra with standard solutions. In the concentration range of interest, *e.g.*, 1–5 m*M*, Beer's law was found

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Table I. Gas Phase Chromatographic Analysis

Compound	Instrument[a] (column)[b]	Temp, °C[c]	Flow rate, ml/min[d]	Retention time, min
H_2, N_2, O_2, CO, CH_4, CO_2	V-A A90 (Pac Q)	~25	~80 (He or N_2)	0.38, 0.51, 0.51, 0.63, 0.82, 6.5
$C_6H_5CH_2COOCH_3$,	MT 2000 (OV-17)	110	35	5.4
n-$C_{10}H_{21}COOCH$				8.2
$(C_6H_5CH_2)_2$,	MT 2000 (OV-101)	160	20	5.7
$(C_6H_5)_2$				3.6
$C_6H_5CH_2COOH$	A200 (FFAP)	75–250 (8.2/min)	26	6.8
$(C_6H_5CH_2)_2$,				4.6
$C_6H_5CH_2CH_2OH$,				3.6
$C_6H_5CH_2COOCH_3$				2.9
$C_6H_5CH_2COOH$,	A200 (FFAP)	75–250 (20/min)	26	4.2
$(C_6H_5CH_2)_2$,				2.7
$C_6H_5CH_2C(CH_3)_2OH$,				1.8
$((CH_3)_2COH\text{-})_2$				1.1
$C_6H_5CH_2C(CH_3)_2OH$	A200 (SE-30)	75–200 (10/min)	20	2.7
$C_6H_5CH_3$,	A200 (SE-30)	48	20	4.2
$(HOCH_2)_2$	(FFAP)	130	22	3.0
$HCOOCH_3$	V-A A90 (CW-fb)	40	50 (He)	0.8
C_6H_5CHO	A200 (CW-cw)	140	20	3.8

[a] Chromatograph: A200 or Aerograph (flame ionization) Model 200; V-A A90 or Varian Aerograph (thermal detector) Model A90; MT 2000 or Micro Tek (dual flame ionization) Model 2000R. [b] Columns: Pac Q or Porapac Q polymer beads, 120–150 mesh, in 0.25 in. × 5 ft aluminum; OV-17 or 5% OV-17 on Anachrom ABS, 70–80 mesh, in 0.25 in. × 5 ft aluminum; OV-101 or 5% OV-101 on Anachrom ABS, 70–80 mesh, in 0.25 in. × 4.25 ft aluminum; FFAP or 5% FFAP on Veroport S, 70–80 mesh, in 1/8 in. × 5 ft stainless steel; SE-30 or 5% SE-30 on Chromosorb W; CW-fb or 5% Carbowax 20M on firebrick in 0.25 in. × 4 ft aluminum; CW-cw or 5% Carbowax 20M on Chromosorb W 1/8 in. × 5 ft stainless steel. [c] Programmed changes are given in parentheses. [d] The carrier gas was usually nitrogen, although helium was also used, as indicated in this table and in the text.

to hold. In the presence of **1** or **2**, *ca.* 1 ml of 0.5 M NaOH was added to a 1-ml sample to form the salt, after which the solution was extracted with 5 ml of spectrograde cyclohexane. Since extraction does not produce complete recoveries, standard solutions of BB or toluene and **1** were prepared and extracted. In this manner, similar recoveries were made from both standard and sample solutions. Since interferences by traces of extraneous material could easily occur in this type of analysis, the shapes of the absorption spectra were examined carefully to see if variations were occurring. The uv results were checked against gpc analyses for BB and toluene; agreement was within 5%.

Gas Chromatographic Analysis. Most of the details are given in Table I. The exit line from the irradiation vessel was attached to a gas sampling valve on the V-A A90 chromatograph and 1-ml injections of gas were sampled. When helium was swept through both the irradiation vessel and the chromatograph, only a slight shift in base line was noted during injections. Gases eluted in the order hydrogen, nitrogen and oxygen together, followed in turn by carbon monoxide, methane, and carbon dioxide. Since all of the gases, except carbon dioxide, gave very narrow peaks, comparisons with known quantities of gas were made by peak height instead of area. The peak heights were calibrated using a synthetic gas mixture (Matheson Co.) containing 0.51% carbon monoxide and 1.0% carbon dioxide in helium. Other mixtures were prepared by injecting quantities of pure gas with a 1-ml gas-tight syringe into a 100-ml bulb containing helium at atmospheric pressure. The gas mixture was then pushed through the gas-sampling valve by displacement with mercury from an attached bulb.

In a typical experiment, the solution to be irradiated was purged with helium at a constant rate, as measured by a soap bubble meter. At 5-min intervals, 1-ml aliquots of gas were injected into the chromatograph. The percentage of each gas in the sample was determined by comparison of peak heights with standards. Knowing the average flow of gas during the intervals, we could calculate the amount of each component swept from the sample. Hydrogen, like helium, has a low thermal conductivity and gives a very weak response in a thermal conductivity detector, when balanced against helium; good sensitivity, however, can be obtained by balancing it against nitrogen. In testing for hydrogen, prepurified nitrogen was used both as a carrier in the gas chromatograph and as a purge through the solution to be examined. In this manner, as little as 0.01% hydrogen could be detected.

The rate at which each gas was displaced from the irradiation vessel was variable. Carbon monoxide with a low solubility in methanol was displaced in *ca.* 5 min, whereas carbon dioxide, being much more soluble,[11] required up to 2 hr to remove.

Considerable effort was made to find a precise method of analysis for irradiated solutions of **1**. Suffice it to say that the FFAP gpc column lost efficiency with continued use and that the conversion to and pyrolysis in the injection port of our chromatograph of the tetramethylammonium salt of **1** gave erratic results.[12] Finally, we used a method based more directly on **2**. Ten drops of concentrated hydrochloric acid were added to 5.0-ml aliquots. After *ca.* 2 hr, esterification was complete. An internal standard of 70 μl of methyl undecanoate (>95%) was added to each solution, prior to its injection onto an OV-17 column. The concentrations of **1** in the original samples were determined by comparison of the ratios of the peak heights and peak areas with standard solutions; both peak height and peak area ratios were linear functions of [**1**] or [**2**].

Since the spectroscopic method previously described suffered from a lack of specificity, a gpc separation on OV-101 was used for BB. At [BB] > 1 mM, an internal standard of biphenyl proved adequate. However, at lower concentrations, tailing of the solvent methanol peak interfered with the internal standard so that none was used. By using care, reproducible standard injections were obtained. A calibration curve showed a linear response between peak height and concentration. When bibenzyl was determined at the 5×10^{-6} M level, samples were first concentrated in Kaderna Danish evaporators. Typically, 70 ml of methanolic solution was reduced to 2 ml with 98% recovery.

Miscellaneous Tests. The gpc data for several photoproducts are given in Table I. Phenylethyl alcohol was also separated by preparative gpc and confirmed by nmr and ir analysis. Formic acid was converted to the methyl ester, then separated by gpc. Formaldehyde was removed from the higher boiling materials by evaporation. The aldehyde was then identified by the "Chromotopic Acid Test".[13] Another colorimetric test utilizing 2-hydrazinobenzothiazole[14] was rejected due to interferences by the other photoproducts.

To test for glycolic acid, the irradiated solutions were made basic with ammonia and heated to dryness at *ca.* 100° to drive off methanol and any formaldehyde. The residue was treated with several drops of concentrated sulfuric acid to convert glycolic acid to formaldehyde. This was then tested with chromotropic acid, and a

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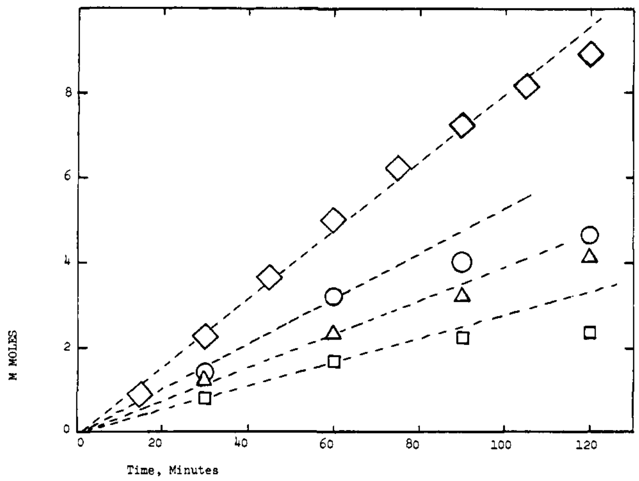

Figure 2. Products of the photodecomposition of phenylacetic acid, 0.0734 *M* in methanol: carbon monoxide, □; bibenzyl, △; carbon dioxide, ○; decrease in acid titer, ◇.

positive violet-red color was obtained.[13] In a more specific test, the irradiated solutions were processed so as to convert any possible glycolic acid to its methyl ester. Even though an authentic sample produced a prominent gpc peak, none was found in the irradiated solutions. It is doubtful, therefore, that glycolic acid is formed in the photolytic reactions.

Benzaldehyde, when present, was identified by its characteristic odor, uv spectrum in hexane, and gpc retention time.

The acidic polymer, which was formed in the irradiations of solutions of **1**, was difficult to characterize. A light yellow sticky solid was obtained by basic extraction of an irradiated solution, followed by acidification and extraction of the lower molecular weight acids with cyclohexane. The material was soluble in methanol and eventually hardened to a clear, yellow solid as the methanol evaporated. A similar solid was precipitated, when **1** was irradiated in cyclohexane, and was characterized as follows: equiv wt 180; ir (KBr) 3300–2800, 1750–1650, 1300–1100 cm^{-1} (all broad); nmr (CCl_4) δ 0.9–4.0 (broad), 3.6 ($ArCH_2$), 7.3 (C_6H_5), 5.2–6.5 (HO_2C, broad). *Anal.* Found: C, 67.49; H, 6.84.

Results and Discussion

Flash photolysis of both **1** and **2** in methanol produced B with λ_{max} at 314 and 302 nm. Our spectrum differs from the usual ones[15] in that our B spectrum appears to be superimposed on a broad characterless absorption which increases in intensity toward shorter wavelengths. Both absorptions decayed within 200 μsec.

Phenylacetic acid was irradiated continuously in several solvents. Judging from its spectrum and from the lamp output, radiant energy was absorbed from *ca.* 280 nm to the cutoff by the Vycor filter at *ca.* 210 nm. Absolute methanol was found to be convenient, since all the starting materials and photoproducts were soluble in it. In addition, methanol enters into several characteristic radical reactions which were helpful in identifying portions of the photocleavage mechanisms.

In Table II are listed the quantum yields (Φ) of a number of products of the photodecomposition of **1** in helium-saturated methanol or in 2-propanol. These Φ's were calculated from initial slopes of formation curves extrapolated to the initial photolysis conditions, where the acid is absorbing all the light. As the photoproducts are formed, they absorb increasing amounts of the incident light resulting in a falling rate of acid decomposition (Figure 2).

Table II. Photoproducts of the Steady Irradiation of 0.0734 *M* Phenylacetic Acid (**1**) or Methyl Phenylacetate (**2**) in Helium-Saturated Solution[a]

Product	**1** in CH_3OH Found	**1** in CH_3OH Φ(26°)	**1** in i-C_3H_7OH Found	**1** in i-C_3H_7OH Φ(25°)	**2** in CH_3OH Found	**2** in CH_3OH Φ(31°)
Decrease in **1** or **2**	+	0.131			+	0.099
Acid titer decrease	+	0.085[b]	+	0.047		
CO_2	+	0.037	+	0.025	+	0.020
CO	+	0.013	+	0.009	+	0.028[d]
H_2	−	$\ll$0.001	−	$\ll$0.001	−	$\ll$0.001
CH_4					+	0.009[d]
$(C_6H_5CH_2)_2$	+	0.029	+	0.02[c]	+	0.02
$C_6H_5CH_2CH_2OH$	+	0.005			+	0.01
$C_6H_5CH_3$	+	~0.002				
HCO_2H	+	<0.01				
CH_2O	+				+	
$(CH_2OH)_2$	+					
$HOCH_2CO_2H$	−					
C_6H_5CHO	−[e]					
$(CO_2H)_2$	−					
$C_6H_5CH_2OH$	−					
$C_6H_5CH_2C(CH_3)_2OH$			+	0.04[c]		
$((CH_3)_2COH)_2$			+	0.01[c]		
$C_6H_5C_2H_5$					−	

[a] The product was identified (+) or sought and not found (−); a blank indicates that the test was not made. The Φ values are initial yields based on light intensity of 1.2 × 10^{19} quanta/sec between 210 and 280 nm. [b] Average of results at ~20 and ~33°. [c] Estimated values. [d] Calculated from ratios to CO_2 at ~15°. [e] + when oxygen is present.

Most of the Φ's listed in Table II are actually average values. More than 16 irradiations were made for **1** in methanol under the specified conditions, and different groups of photoproducts were sought during each experiment. For example, Φ(CO_2) is the average of eight results, whereas Φ for phenylethyl alcohol is the average of three results. Most tests, except for toluene, were performed more than twice.

Even though gas recoveries were usually greater than 90%, Φ(CO_2) in Table II should nevertheless be considered a minimum value. Φ(CO_2) varied appreciably with the temperature of the irradiated solution. At ~15°, Φ = 0.026, while at 33°, Φ increased to 0.045. Since all recoveries were carried out at ~25°, these differences are not due to variation in experimental technique. The decrease in acid titer was the only other parameter tested which exhibited such a marked variation with temperature, *i.e.*, 0.071 at *ca.* 20° and 0.099 at 33°. Besides unreacted **1**, substantial amounts of acidic polymer and small quantities of other acidic products contributed to the acid titer.

Only small decreases in Φ at lower temperatures were noted for the amount of **1** decomposed and the amount of BB formed. In fact, the yield of BB was essentially constant and showed little variation between different irradiations. However, the Φ's of phenylethyl alcohol varied more among different tests, which may indicate a dependence on mixing rate, temperature, etc. This, however, was not explored further. Benzaldehyde was not produced when the irradiations were carried out in the absence of oxygen; when pure oxygen was bubbled through the methanolic solutions, this aldehyde attained a steady-state concentration of *ca.* 0.5 m*M*, though it too appeared to be undergoing photolytic decomposition.

Flash photolyses of solutions of **1** indicate that its decomposition produces B. Of the several mechanisms

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considered, two primary pathways appear to be most consistent with our observations (Table II). Following excitation, **1*** apparently undergoes homolytic cleavage to form either a carboxyl or hydroxyl radical, as in eq 1. The relative unimportance of cage recombination in this as well as in related systems[4,16] suggests that collisional deactivation of **1*** accounts for the low value $\Phi = 0.13$ for the decomposition of **1**.

A third mode of carboxyl cleavage, namely to form a hydrogen atom (eq 1c), is ruled out by the absence of hydrogen atom reactions. If hydrogen atoms were formed along (1c), they would either add to the aromatic acid or abstract hydrogen from the solvent. By considering the absolute rate constants (M^{-1} sec^{-1})

$$H\cdot + C_6H_5CH_2CO_2H \longrightarrow \cdot C_6H_6CH_2COOH \quad k = 1.0 \times 10^9 \qquad (2)$$

$$H\cdot + CH_3OH \longrightarrow H_2 + \cdot CH_2OH \quad k = 1.6 \times 10^6 \qquad (3)$$

for these reactions,[17] and allowing for differences in concentration, we calculate that about one in three hydrogen atoms should be trapped by the methanol and would produce hydrogen, as in eq 3.

In 2-propanol, the amount of hydrogen abstraction should be at least as large since reaction with hydrogen atoms is even faster.[18] The absence of all but trace amounts of hydrogen gas indicates that step 1c is not a significant cleavage path.

A fourth primary process, namely photoionization (1d), must be considered. At pH 8.4 in water, flash photolysis of the anion of **1** produces the hydrated electron and B.[2] At its natural pH in methanol, flash photolysis of **1** yields B, but we detected no solvated electron. Since the photo- or pulse radiolysis yields of solvated electron from some organic molecules are often lower in alcohols than in water,[2,19,20] it is still conceivable that the solvated electron was a transient in our system. In the presence of methanol and **1**, however, this species would produce hydrogen atoms.[20] Since we have no evidence for these, we also rule out the solvated electron, and thus step 1d.

Other photoionization sequences, *e.g.* (1e), can also be rejected. It has been found that in methanol, phenylacetate ion decarboxylates to give toluene, presumably *via* the benzyl anion.[4] Since the yields of toluene from **1** were insignificant, dissociation of **1** to give the anion and hydrogen ion, either before or after excitation, does not seem to be important.

Consider in turn the fate of the first products. Benzyl radicals formed in (1a) and from decarbonylation of the phenylacetyl radical in (1b) ($\Phi \leq 0.065$) lead to BB. The high yield of BB ($\Phi = 0.058$ as B) indicates that, for the most part, B recombines *selectively* at rates (k_R) that are less than diffusion rates.[4,21] Alternatively the other radicals formed in initially equal concentrations generally do not scavenge B above $\Phi = 0.007$. Moreover, reported values of k_R are consistent with this selectivity.[4,21] Apart from the uncertainty in Φ and in k_R, any analysis for the present system can only be semiquantitative, since we have no sure way of knowing how many (if any) B's have been trapped by the polymer, except that $\Phi \leq 0.02$ for this diversion (see below).

$$\underset{\text{B}}{2C_6H_5CH_2\cdot} \longrightarrow \underset{\text{BB}}{C_6H_5CH_2\text{–}CH_2C_6H_5} \quad k_R = (3\text{–}20) \times 10^8 \qquad (4)$$

On path 1a, we have proposed the formation of the carboxyl radical, chiefly for supportive and indirect reasons. Admittedly, we have the observation of a broad absorption underlying the spectrum of B during the flash photolysis of **1**; this background was transient and appeared to be the end absorption of a peak at shorter wavelengths (<300 nm); for carboxyl, ϵ 3000 M^{-1} cm^{-1} at $\lambda_{\max}$ 235 nm.[22a,b] If carbon dioxide were formed in a primary process, temperature changes should have little effect on its yield. The increased yields of carbon dioxide at higher temperatures may be evidence for a secondary reaction, *e.g.*, from carboxyl radical. But the major role of carboxyl in our scheme (1) is that it provides a plausible alternate to the formation of hydrogen atoms and eventually of molecular hydrogen. Moreover, the carboxyl radical is a primary product of the thermolysis of **1**; such studies have, in fact, led to an assignment of the dissociation energy of the benzyl to carboxyl bond, $D(C_6H_5CH_2\text{–}COOH) = 55$ kcal/mol.[23]

Dissociation of the carboxyl radical to carbon dioxide and a hydrogen atom is endothermic by *ca.* 8 kcal;[24] hydrogen transfer, *e.g.*, to oxygen, methylene blue, oximes, radicals, etc., occurs readily.[22] In eq 5–10 we indicate some of the possibilities citing rate and thermochemical data[24] and using the broken arrow ($\not\longrightarrow$) for reactions not observed by us. In our system, hydrogen transfer from carboxyl to **1** (eq 5a) is exothermic, and

$$\begin{aligned} \cdot CO_2H + \mathbf{1} &\xrightarrow{a} \cdot C_6H_6CH_2COOH + CO_2 \quad \Delta H \simeq -21 \\ &\xrightarrow{b} \cdot C_6H_5(OH)CH_2COOH + CO \end{aligned} \qquad (5)$$

$$\begin{aligned} \cdot CO_2H + CH_3OH &\xrightarrow{a} HCO_2H + \cdot CH_2OH \quad \Delta H \simeq -4 \\ &\not\xrightarrow{b} CO_2 + H_2 + CH_2OH \quad \Delta H \simeq 0 \qquad (6) \\ &\xrightarrow{c} CO + H_2O + \cdot CH_2OH \quad \Delta H \simeq 0 \end{aligned}$$

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(24) In this paper all cited rate constants have the units M^{-1} sec^{-1}; all enthalpies of reaction, ΔH, have the units kcal/mol. Gas-phase values of $\Delta H_f{}^\circ$ in kcal/mol have been taken from S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, Appendix, and D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969), except as indicated: **1** (−75),[23] **2** (∼−62),[25a] CH_3OH (−48), CO_2 (−94), CO (−26), H (52), HO (9), HO_2 (5), HCO (7), CH_3O (3.5), HCO_2 (−36), CO_2H (−51), HCO_2H (−91), CO_2CH_3 (−52),[25b] CH_2OH (−4), $C_6H_5CH_2$ (45), CH_3 (34), CH_3OH (−48), C_6H_6 (20), 1,3-cyclohexadiene (26), 1,3-cyclohexadienyl (43), C_6H_5 (80), $(COOH)_2$ (−184), $C_6H_5CH_3$ (12), $(CH_3)_2C(OH)$ (−27), $H_2O(l)$ (−68), $HCOOC_2H_5$ (−84).

(25) (a) Our estimate based on ref 23 and I. Wadsö, *Acta Chem. Scand.*, **12**, 630 (1958); (b) J. C. J. Thynne, *Trans. Faraday Soc.*, **58**, 676 (1962).

$$\begin{aligned} \cdot CO_2H + RH &\xrightarrow{a} HCO_2H + R\cdot \\ &\xrightarrow{b} CO + H_2O + R\cdot \end{aligned} \quad (7)$$

$$\begin{aligned} \cdot CO_2H + \cdot CO_2H &\xrightarrow{a} HCO_2H + CO_2 \quad \Delta H \simeq -83 \\ &\xrightarrow{b} (CO_2H)_2 \quad \Delta H \simeq -82 \\ &\xrightarrow{c} CO + H_2O + CO_2 \quad \Delta H \simeq -86 \end{aligned} \quad (8)$$

$$\begin{aligned} \cdot CO_2H + \cdot CH_2OH &\xrightarrow{a} HO_2CCH_2OH \quad k = 5 \times 10^8 \\ &\xrightarrow{b} CO + CH_2(OH)_2 \end{aligned} \quad (9)^{22e}$$

$$\cdot CO_2H + OH\cdot \longrightarrow (H_2CO_3) \longrightarrow H_2O + CO_2 \quad (10)$$

subsequent transfers to the product of eq 5 should be even more so. There are a number of apparently acceptable steps for the formation of carbon dioxide, *e.g.*, eq 5a, 8a, and 10, and for formic acid, *e.g.*, eq 6a, 7a, and 8a, but we believe that the radical–radical reactions (eq 9, 10) are less probable. Unfortunately, Φ for formic acid is not precise, but it does help to account for the observed excess of benzyl material over $\Phi(CO_2) + \Phi(CO)$ in Table II.

It appeared to us that the detection of carbon monoxide ($\Phi = 0.13$) as a photolytic product virtually required step 1b. Evidence for the formation of the phenylacetyl radical in the photolysis of dibenzyl ketone, followed by its decarbonylation,[16] parallels this sequence. A referee, however, suggested that we also consider the carboxyl radical as a possible source of carbon monoxide, *e.g.*, eq 5b, 6c, 7b, 8c, and 9b. Although this is an interesting idea, the recent literature contains no evidence that the carboxyl radical behaves as a hydroxylating agent and gives rise to carbon monoxide, at least when generated thermally, chemi-

$$\cdot COOH \longrightarrow CO + OH \quad \Delta H = 34 \quad (11)$$

cally, by pulse radiolysis, or by other irradiation techniques.[22] Since it is not evident whether our photochemically produced carboxyl radical was in the ground state, or that carbon monoxide was actually sought and not found when carboxyl was generated by other means, the details of the generation of carbon monoxide remain unsettled. Therefore, we write $\Phi_a/\Phi_b \leqslant \Phi(CO_2)/\Phi(CO)$ for eq 1, but we are inclined to believe that these ratios are, in fact, equal and shall proceed on this basis.

If $\Phi = 0.065$ represents the sum of reactions 1a and 1b and $\Phi(CO) = 0.013$ represents the amount of reaction 1b, then $\Phi_a/\Phi_b \simeq 4$. This preference may be influenced by the relative stability of the products in the primary process 1a. It is surprising, however, that this preference is not greater, when we consider that both types of processes are of almost equal importance in the photolysis of acetic acid.[26]

$$\cdot OH + CH_3OH \longrightarrow H_2O + \cdot CH_2OH \quad k = 8.7 \times 10^8 \quad (12)$$

$$\cdot OH + \mathbf{1} \longrightarrow (HOC_6H_5CH_2COOH)\cdot \quad k \simeq 8 \times 10^9 \quad (13)$$

$$B + \cdot CH_2OH \longrightarrow C_6H_5CH_2CH_2OH \quad (14)$$

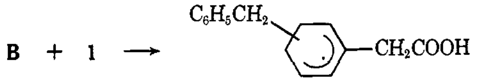
$$HOCH_2\cdot + \cdot CH_2OH \longrightarrow HOCH_2CH_2OH \quad k \simeq 1 \times 10^9 \quad (15)$$

$$R\cdot + \cdot CH_2OH \longrightarrow RH + CH_2O \quad (16)$$

$$\mathbf{1} + \cdot CH_2OH \longrightarrow (HOCH_2C_6H_5CH_2COOH)\cdot \quad (17)$$

In eq 1b, the hydroxyl radical should be quickly scavenged by methanol (eq 12)[27] and perhaps by **1** (eq 13).[17b] Because of the low yield of BB (4%) reported for the hydroxyl-induced decarboxylation of **1** in water at pH 6, we can rule this process out.[28] Likewise, cage or random recombination to form benzyl alcohol appears to be unimportant ($\Phi = 0$). Hydroxymethyl radicals appear to be much more reactive than B; they combine to give glycol (eq 15) and possibly transfer hydrogen to yield formaldehyde (eq 16).[17,29] Hydroxymethyl radicals combine with B to give phenylethyl alcohol (eq 14). There is also the possibility that the hydroxymethyl radical may add to **1** (eq 17), although this has been shown to be a slow reaction.[17]

One of the end products of the photolysis of **1** is a complex polyacid (see Experimental Section). Equations 5, 13, and 17 could be the initiating steps in its formation. It might appear that eq 18 should be included too, but it turns out that B prefers to form BB (eq 4), when it is generated from, and in the presence of, a large variety of simple aromatic species; B is captured, however, by some condensed hydrocarbons, *e.g.*, anthracene, pyrene, etc.,[30] and may well be caught *after* the initiating steps. In this regard, it is interesting that the thermolysis of di-*tert*-butyl peroxide at ~150° in the presence of **2** and 1-decene leads to 2-phenyldodecanoate and some *meso*-α,α'-dicarbomethoxybibenzyl; photolysis appears to be far less effective in promoting these radical reactions.[31]



(18)

The radical adducts in eq 5, 13, or 17 may disproportionate, dimerize, attack **1** or another radical, be photolyzed, etc. Some semireduced aromatics, *e.g.*, biphenyl, disproportionate or dimerize at comparable rates.[32] The product pattern in Table II indicates that roughly two molecules of **1** are decomposed ($\Phi = 0.131$) for every benzyl moiety isolated ($\Phi = 0.065$). The nmr spectrum of the polymer indicates a high degree of reduction even though some benzyl groups are still evident.[1] The equivalent weight of *ca.* 180 as compared to 136 for **1** also indicates that some nonacid groups, *e.g.*, benzyl, hydroxymethyl, have been incorporated. If we take $\Phi = 0.066$ as the unaccounted loss in **1** and $\Phi = 0.131 - 0.085 = 0.046$ as a measure of the units of **1** (mol wt 136) in the polymer, then $\Phi = 0.020$ would be the figure for the decarboxylated or neutral units of **1** (mol wt 92). This leads to an equivalent weight in the polymer of $136 + 92(0.02/0.046) \simeq 177$, which is fortuitously close to the value we found.

A limited number of irradiations of **1** in other solvents were carried out. In aqueous solutions, the solutions turned milky white due to the formation of BB, and the lamp jacket became coated with polymer which absorbed the light. For this reason, irradiations could not be carried on long enough to obtain any additional information. A similar situation occurred in cyclohexane, except that BB remained in solution and rela-

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Table III. Primary Cleavage Modes of the Carboxyl Function, RCH_2COOR' or $R''(CH_2)_3COOR'$[a]

1[b]	$RCH_2\cdot$	$COOR'\cdot$	14[f]	$RCH{=}C{=}O$			HOR'
2[c]	RCH_2^+	$COOR'^-$	15	$RCH_2\cdot$	CO_2		$R'\cdot$
3	RCH_2^-	$COOR'^+$	16	RCH_2^+	CO_2		R'^-
4[d]	$RCH_2CO\cdot$	$OR'\cdot$	17	RCH_2^-	CO_2		R'^+
5	RCH_2CO^+	OR'^-	18	$RCH_2\cdot$	CO		$OR'\cdot$
6[e]	$RCH_2COO\cdot$	$R'\cdot$	19	RCH_2^+	CO		OR^-
7	RCH_2COO^-	R'^+	20	$RCH_2CO_2\cdot$	e^-		R'^+
8[c]	RCH_2COO^+	R'^-	21	RCH_2CO^+	$OR\cdot$		e^-
9	$RCH_2COOR'^+$	e^-	22	$RCH_2\cdot$	CO_2	e^-	R'^+
10[f]	RCH_2R'	CO_2	23	RCH_2^+	CO_2	e^-	$R'\cdot$
11[g]	RCH_2OR'	CO	24	RCH_2^+	CO	$OR'\cdot$	e^-
12[h]	$CH_2{=}C(OR')OR$		25	RCH_2^+	$COOR\cdot$	e^-	
13[i]	$R''CH{=}CH_2$	$CH_2{=}C(OH)OR'$					

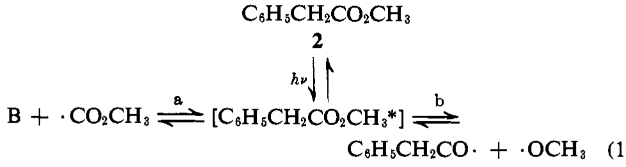
[a] R, R', or R'' may be H. One or more of the fragments may be in an excited state (*). [b] α-Cleavage in **3**; eq 1a and 19a. [c] Improbable. [d] β-Cleavage in **3**; eq 1b and 19b. [e] γ-Cleavage in **3**. [f] Four-center elimination. [g] Sigmatropic shift [1,2]. [h] Sigmatropic shift [1,3]. [i] Norrish, type II split.[34]

tively "pure" polymer was deposited. No trace of toluene was found. In 2-propanol the solutions would darken and take on a slight yellow coloration. Although the Φ's were slightly lower than for methanol, the carbon dioxide to carbon monoxide ratio was still 2.8/1 (Table II). Tests for molecular hydrogen showed that $\Phi \simeq 0$. Bibenzyl and analogs of the methanol products, that is, 2,2-dimethylphenylethyl alcohol and pinacol, were formed. The Φ's for these three photoproducts were estimated incidentally from a typical run for BB; the relative Φ's are more certain than the absolute Φ's.

Since the α,α-dimethylhydroxylmethyl radical should be more stable than the hydroxymethyl radical, we might expect a higher proportion of these radicals to react with B instead of combining to form pinacol. What we found, in fact, was that Φ for 2,2'-dimethylphenylethyl alcohol was roughly twice the Φ for BB, which is what might be expected on a statistical basis.

The photocleavage of **2** in methanol was also studied briefly (Table II). The ester was found to decompose with *ca.* 75% the efficiency of the free acid. The carbon dioxide to carbon monoxide ratio fell to 0.7. Significant amounts of methane were detected, whereas hydrogen yields were still negligible. Lower yields of BB were observed than from **1** and twice as much phenylethyl alcohol was found. No ethylbenzene was found after an irradiation, although it was sought. Formaldehyde was detected, but not quantitated during this work. During a typical irradiation, the solution would turn yellow, reminiscent of the polymer formed during decomposition of **1**.

The changes in the photochemistry from **1** to **2** cannot be ascribed to gross differences in energy absorbed, since the absorption spectra of both materials are strikingly similar (Figure 1). Of the several mechanisms considered, one involving two primary dissociation processes, as in eq 1, appears to best explain the observed photoproducts



$$\begin{tikzcd} & C_6H_5CH_2CO_2CH_3 \ \mathbf{2} \arrow[d, shift right, "h\nu"'] & \\ B + \cdot CO_2CH_3 \arrow[r, leftharpoondown, shift right] & \left[C_6H_5CH_2CO_2CH_3^*\right] \arrow[l, "a"', shift right] \arrow[u, shift right] \arrow[r, "b"] & C_6H_5CH_2CO\cdot + \cdot OCH_3 \arrow[l, shift left] \end{tikzcd} \quad (19)$$

The product yields indicate that, unlike **1**, β cleavage is the preferred path of **2**. The ratio Φ_a/Φ_b is now equal to *ca.* 0.8, or ~0.2 of the value of the ratio for **1**.

Clearly, the major primary process during photolysis of **2** involves scission of the C–O bond. This process may be favored by formation of the methoxyl radical which is more stable than the hydroxyl radical. The scavenging reaction of methanol should still occur.

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH \quad \Delta H = -8 \quad (20)$$

The carboxymethyl radical formed in reaction 19a is relatively unstable at room temperature; dissociation into carbon dioxide and a methyl radical is exothermic, while other steps, *e.g.*, hydrogen abstraction or methoxyl

$$\cdot COOCH_3 \longrightarrow CO_2 + CH\cdot \quad \Delta H = -8 \quad (21)$$

transfer, tend to be endothermic

$$\cdot COOCH_3 + CH_3OH \begin{cases} \xrightarrow{a} HCOOCH_3 + \cdot CH_2OH \quad \Delta H = 13 \\ \xrightarrow{b} CO + CH_3OH + \cdot CH_2OH \quad \Delta H = 22 \end{cases} \quad (22)$$

Methyl radicals formed in eq 21 lead to methane through hydrogen abstraction from the solvent methanol. Even though hydrogen abstraction from **2** is known (eq 24),[33] and the rate of such abstraction by

$$CH_4 + \cdot CH_2OH \xleftarrow[a]{CH_3OH} \cdot CH_3 \xrightarrow[b]{+2} CH_3\dot{C}_6H_5CH_2COOH \quad (23)$$

$$\mathbf{2} \xrightarrow[\Delta]{(RO)_2} C_6H_5CH(COOH)\cdot \xrightarrow{RCH{=}CH_2} RCH_2CH_2CH(COOH)C_6H_5 + (C_6H_5CH(COOH))_2 \quad (24)$$

methyl radicals is two to four times faster from toluene than from methanol,[34] most of the radicals should react with the solvent in preference to abstracting a benzylic hydrogen of **2** due to the large concentration difference. Since the yield of methane is much less than the yield of carbon dioxide, there must be a competing reaction for the methyl radicals. A likely reaction is addition to the aromatic ring of the ester (eq 23b). At this point, the description of the system, *e.g.*, the formation of formaldehyde or polymer, the fate of unstable intermediates, etc., should very much resemble that for **1**.

Primary Cleavage Mechanisms. In Table III, we have set out many of the possible first products of photolysis of a carboxyl function. These have been

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(33) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955, p 201.

(34) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, 93, 2685 (1971).

grouped according to single cleavage (1–9), molecular reaction (10–14), and multiple cleavage (15–25). The binary pairs in 1–9 can, of course give rise to the more numerous products of 15–24; indeed, the simultaneous concentration of sufficient energy in two or more bonds which is required to give the third group seems inherently less probable than having the products arise from further fragmentation of the group 1 species. Although distinctions between decompositions from excited states, *e.g.*, singlet *vs.* triplet, etc., are not made here, these will certainly have to be established too.[34]

In their survey, Calvert and Pitts documented most of the homolytic and molecular processes and one polar example (17) of Table III.[5a] However, one can no longer neglect the heterolytic paths: the photodecarboxylations of phenylacetate ion[4] and the nitrophenylacetic acids[7] produce benzylic anions; the photohydrolyses of methoxybenzyl ester produce benzylic cations.[35] Since the thermal decomposition of phenylacetyl and other diacyl peroxides has been shown to proceed by both a polar as well as a radical route,[36] we believe that similar competitive processes should be found in the photolyses of these compounds. The ejection of an electron by photoionization, according to 9 in Table III, is known from mass spectroscopic and flash photolysis studies.[2] The detection of additional species, *e.g.*, B, in aqueous solutions of **1** indicates that 22 was observed.[2] In fact, the examination of new systems and the reexamination of old ones for both the solvated electron and coproducts should turn up examples in the group 21–25. To summarize, perhaps one-third to one-half of the entries in Table III remain hypothetical; of the recognized cleavage modes, a relatively small number has been characterized and understood even at the semiquantitative level of (or beyond) the present work.

In the light of Table III, the photocleavage mechanisms of **1** and **2** might appear to be very simple. The primary steps, at least, essentially involve only the carboxyl function. The α and β homolyses (1, 4) indicated in **3** predominate. It is difficult, however, to rationalize this preference by using thermochemical data relating to overall product stabilities. For if these were critical, then the molecular reactions leading to stable molecules (10–14) would normally be observed. We do know that the activation energy for α and β cleavage is $\sim$ 55 kcal/mol,[23] which makes these kinetically accessible. Beyond this, it would seem that further photolysis studies of **1** and **2** with narrower energy ranges,[5a] *e.g.*, in the n–π^* region (200–250 nm), in the π–π^* region (250–275 nm), with sensitizers (>275 nm), etc., may lead to fewer products and even greater understanding of the primary processes.

Acknowledgment. We are grateful to Professor L. I. Grossweiner and his associates for assistance with the flash photolysis measurements and to the Lake Michigan Basin Office of the Federal Water Pollution Control Administration for making their Micro Tek Chromatograph available to us.

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A Probable Diffusion-Limited Mechanism in the Hydrolysis of a Thiolester

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Abstract: The hydrolysis of methyl *S*-trifluoroacetylmercaptoacetate is subject to general base catalysis. The Brønsted β is near zero for catalysis by eight carboxylate anions varying in pK_a from 2.1 to 4.3. No catalysis could be seen by trifluoroacetate ion, indicating the value of β must increase sharply for catalysts with pK_a's near zero. Similar behavior is observed for weakly basic amine catalysts. The results are interpreted in terms of a rate-determining, diffusion-limited deprotonation of a zwitterionic intermediate formed by the uncatalyzed addition of water to the thiolester.

Fedor and Bruice[1] found hydrolysis of ethyl trifluorothiolacetate proceeds by a general base catalyzed formation of an anionic intermediate and its uncatalyzed breakdown. Calculations based on assumptions as to the pK_a of the intermediate and the equilibrium constant for its formation from the thiolester indicated that the rate constants for the partitioning of the anionic intermediate to thiolester and products is within 10–100 of the diffusion limit.[2] Preliminary data on the more reactive thiolester ethyl *S*-trifluoroacetylmercaptoacetate indicated that breakdown of the anionic intermediate formed in the hydrolysis of this ester to give starting materials is diffusion limited.[2] The purpose of this paper is to present further evidence that the hydrolysis of this ester and its more water soluble methyl analog is diffusion limited.

Experimental Section

Materials. Commercially available carboxylic acids and amines were purified by distillation or recrystallization. Samples of 2,2′,2′′-tricyanotriethylamine and 2-hydroxy-2′,2′′-dicyanotriethyl-

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[2] R. Barnett and W. P. Jencks, *J. Org. Chem.*, **34**, 2777 (1969).