The Photodecarboxylation of Nitrophenylacetate Ions

J. David Margerum and Cunegunda T. Petrusis

Contribution from the Hughes Research Laboratories, Malibu, California 90265.
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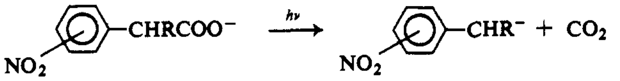
Abstract: These studies characterize the primary process and products in the photodecarboxylation of nitrophenylacetate ions in aqueous solutions. 3-Nitrophenylacetate, 4-nitrophenylacetate, and 4-nitrohomophthalate ions decarboxylate with a quantum yield of about 0.6 at 367 nm, while that of *o*-nitro structures (2-nitrophenylacetate and 2,4-dinitrophenylacetate ions) is only 0.04. *aci*-Nitro intermediates are identified spectrally by flash photolyses from the *o*- and *p*-nitro structures, but not from the *m*-nitro structure. Results are consistent with a mechanism of photodecomposition into carbon dioxide and a nitrobenzyl anion which is stabilized as an *aci*-nitro anion in *o*- and *p*-nitro structures. The nitrophenylacetic acids are more stable photochemically than their ions; neither CO_2 nor *aci*-nitro intermediates are observed from photolysis of the undissociated acids. The *aci*-nitro yield varies with pH according to the pK of the acid being photolyzed; thus a pK of 4.8 is calculated for the α-carboxyl group of 4-nitrohomophthalic acid. Three of the *aci*-nitro anions occur *via* photochemical hydrogen-transfer reactions from other compounds so that by comparison with the photodecarboxylations the quantum yields of H-transfer photochromism in 2-nitrotoluene, 2,4-dinitrotoluene, and 5-nitro-*o*-toluate ions are estimated to be about 0.01, 0.003, and 0.07, respectively.

In the course of studies on the photochromism of compounds with nitrobenzyl structures,[1] we noted that an irreversible photochemical decarboxylation occurs in aqueous solutions of compounds with nitrophenylacetate ion structures.[2] In both types of reaction *aci*-nitro intermediates are postulated to occur from photochemical acid–base processes. While the photochromic process appears to be a reversible proton-transfer reaction, the photodecarboxylation mechanism is based upon the formation of carbon dioxide and a carbanion residue, as in eq 1. The carboxyl forms of these nitrophenylacetic acids photodecompose less readily and do not yield the same intermediates or products as their ions.



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In this paper we describe the experimental basis for eq 1, which is different from the behavior of many other carboxylic acids and salts in aqueous solutions. For example, Leermakers and Vesley[3] found that aqueous solutions of pyruvic acid and benzoylformic acid photodecarboxylate readily, while the pyruvate ion shows little or no reaction. Several aliphatic carboxylic acids decompose primarily by homolytic cleavage into free radicals, such as the photolysis of acetic acid in D_2O,[4] butyric acid in water,[5] and phenylacetic acid in a low-temperature glass.[6] Flash photolysis studies[7] of aqueous phenylacetate ion solutions have provided evidence for photooxidation to form solvated electrons, CO_2, and benzyl radicals. Photolyzed acetate ions[8] and butyrate ions[5] have been postulated to react with water to give HCO_3^- and a saturated hydrocarbon as well as other products from competitive free-radical reactions.

Experimental Section

A. Materials. Four nitrophenylacetic acids are commercial samples purified by dissolving in 35A denatured ethanol, treating with Norite charcoal, filtering, and recrystallizing from water–ethanol solutions: 2-nitrotophenylacetic acid and 2,4-dinitrophenylacetic acid are from Eastman, while 3-nitrophenylacetic acid and 4-nitrophenylacetic acid are from Aldrich. 4-Nitrohomophthalic acid is prepared by treating a sulfuric acid solution of recrystallized homophthalic acid with concentrated nitric acid at 0–5° and recrystallizing the crude product from hot water, mp 219° dec (lit.[9] 220° dec). 4,4′-Dinitrodiphenylacetic acid is prepared by the method of Haskelberg and Lavie.[10] The product is purified by crystallization from water, mp 171.5° dec (lit.[10] 170–172.5°).

5-Nitro-*o*-toluic acid is prepared by the method of Giacalone,[11] mp 178.5–179° (lit.[11] 179°). 4,4′-Dinitrobibenzyl-2,2′-dicarboxylic acid is synthesized by mixing 5 g of bibenzyl-2-2′-dicarboxylic acid in 30 cc of concentrated H_2SO_4 at 0–5° and adding over 30 min a mixture of 5 g of KNO_3 in 30 cc of concentrated H_2SO_4. After 30 min below 10° the mixture is dumped on ice, filtered, and recrystallized from acetic acid, mp 305°.

B. Product Identification and Yields. The insoluble products are separated from the photolyzed solutions as a precipitate or by extraction. 2-Nitrotoluene and 3-nitrotoluene are obtained as oils from ether extracts and are identical with Eastman samples on gas chromatography columns. 4,4′-Dinitrobibenzyl is separated as a precipitate, recrystallized from acetone–ethanol, pale yellow needles, mp 181–183° (lit.[9] 180.5°; recrystallized Aldrich sample 182°). Its identity is further confirmed by ir and uv spectra and also by CrO_3 oxidation to 4-nitrobenzoic acid. Ether extracts of 4-nitrotoluene are evaporated, redissolved in CS_2, and identified by gas chromatography. Crystals of 4-nitrotoluene, mp 51–52° (lit.[9] 54.5° (52°)) as well as 4,4′-dinitrobibenzyl are obtained from a solution of 4-nitrophenylacetate ions at pH 8 in a closed flask exposed to room fluorescent lamps for 3 weeks. 2,4-Dinitrotoluene is separated in an ether extract, evaporated, and recrystallized from ethanol–water, mp 68–70° (lit.[9] 70–71°). Photolysis of 4,4′-dinitrodiphenylacetate ions at pH 10 gives a precipitate, recrystallized from ethanol–water, mp >300° (not identified); the products from photolysis at pH 5.9 are extracted with ether and recrystallized from ethanol to give 4,4′-dinitrodiphenylmethane, mp 186–188° (lit.[10] 187°). Photolyzed solutions of 4-nitrohomophthalate ions are acidified and the products separated by differences of solubility in hot water: 5-nitro-*o*-toluic acid is obtained from low-intensity photolysis at

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[1] J. D. Margerum and R. G. Brault, *J. Am. Chem. Soc.*, **88**, 4733 (1966).

[2] J. D. Margerum, *ibid.*, **87**, 3772 (1965).

[3] (a) P. A. Leermakers and G. F. Vesley, *ibid.*, **85**, 3776 (1963); (b) *J. Org. Chem.*, **28**, 1160 (1963).

[4] K. Clusins and W. Schanzer, *Ber.*, **75B**, 1795 (1942).

[5] P. Borrell and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A262**, 19 (1961).

[6] G. Porter and E. Strachan, *Trans. Faraday Soc.*, **54**, 1595 (1958).

[7] L. I. Grossweiner and H. I. Joschek in "Solvated Electron Symposium," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 286.

[8] L. Forkas and O. H. Wansbrough-Jones, *Z. Physik. Chem.*, **B18**, 124 (1932).

[9] "Dictionary of Organic Compounds," 4th ed, Oxford University Press, New York, N. Y., 1965.

[10] L. Haskelberg and D. Lavie, *J. Am. Chem. Soc.*, 71, 2580 (1949).

[11] A. Giacalone, *Gazz. Chim. Ital.*, **65**, 840 (1935).

pH 5.8, acidification, filtration, and recrystallization from the filtrate, mp 176–178°, while an insoluble acid (mp 267–300°) separated from photolysis above pH 10 has an ir spectrum corresponding to 4,4′-dinitrobibenzyl-2,2′-dicarboxylic acid.

The analyses in Table I are carried out on 10 ml of photolyzed solutions. After centrifuging, two 1-ml aliquots are analyzed for carbonate by a micro-diffusion method,[12] using blank runs as correction factors. The 4,4′-dinitrobibenzyl precipitate is washed with dilute base and water, dried, and analyzed either by weight or uv analysis. For uv analysis it is dissolved in hot methanol, cooled, diluted to 500 ml, and measured in a 1-cm cell on the Cary 14 spectrophotometer, ε_{277} 2.15×10^4. 4-Nitrotoluene from the aqueous filtrates is analyzed by uv of the ether extract, ε_{268} $1.01 \times 10.^4$

C. Quantum Yield Studies. The photolysis light source consists of a PEK 200-W high-pressure Hg arc, a Bausch & Lomb 33-86-01 grating monochromator, and a Corning CS 7-37 or CS 7-54 glass filter. The 2-cm diameter beam is incident on a flat Pyrex window of the cylindrical photolysis cell, 6.5-cm diameter and 4-cm path length. The cell has a glass-stoppered side arm for the addition of acid and also a gas-flushing inlet; the outlet is connected to a reflux condenser and leads to a diffuser in a $Ba(OH)_2$ trap. This is a modification of a technique by Anderson.[13] Samples of 100 ml are photolyzed while flushing with N_2 and stirring magnetically; then 3 *N* HCl is added and the solution is heated for 20 min, boiling 5 min. The CO_2 is carried by the N_2 into the trap, which is titrated and compared with a blank run from the same sample. All photolyses are carried to less than 1% decomposition.

The organic products are determined by extraction at pH 10 with diethyl ether. The absorbance at the uv maximum is read in a 1-cm cell on the Cary 14 and is corrected using blank runs. The following extinction coefficients are used for these ether extracts: 2-nitrotoluene, ε_{255} 5.4×10^3; 3-nitrotoluene, ε_{261} 8.2×10^3; combined 4-nitrotoluene and 4,4′-dinitrobibenzyl, ε_{267} 1.06×10^4. The photolyses are carried out with no more than 0.1–1% decomposition.

Light intensities are determined by chemical actinometry with the ferrioxalate actinometer[14] in the same photolysis cell before and after each run on nitrophenylacetate ion samples.

D. Flash Photolysis Studies. A linear 3-in. flashlamp and a 5- or 7-cm sample cell are placed at the foci of a polished elliptical cavity. Usually a CS 7-54 filter is placed between the flashlamp and the cell. The transmission of a sample is monitored using a battery-operated 42-W lamp whose beam passes through selected glass filters, the cell, and a Bausch & Lomb grating monochromator onto a RCA 7326 photomultiplier and is recorded with either a Tektronix 555 oscilloscope or with a Sanborn 7701 recorder. Two flashlamp systems are used. (1) A *millisecond flash system* consisting of a PEK XE1-3 flashlamp is operated with a Hughes Model 350 laser power supply. Normally it is flashed at 1.7 kV with a square-shaped pulse of input energy from 18 J in 0.15 msec up to 360 J in 3.0 msec. In a modified mode, 10 J at 1.2 kV up to 225 J at 6 kV is discharged in less than 80 μsec (25 μsec FWHH (full width at half-height)). (2) A *microsecond flash system* consisting of a PEK XE9-3 xenon flashlamp is used in series with a spark gap which is coaxial with a capacitor (0.05 μF, 20 kV) from a modified Unilectron LSS-022 system. The lamp is flashed by triggering the spark gap, giving a flash ~1–2 μsec in duration and 0.5 μsec FWHH, but the total energy discharged through the spark gap and lamp is only 10 J.

The flash photolysis decarboxylates only 1–2% of the 2-nitrophenylacetate ion solutions, but at lower concentrations as much as 10–20% of the 3-nitro and 4-nitro derivatives can be decomposed per flash. In Figures 4 and 5 the maximum product concentrations are approximately 1×10^{-6} and 5×10^{-7} *M*, respectively, which could alter the pH appreciably only in the 6–8 range, where small concentrations of phosphate buffer are used to offset this effect.

Results

A. Permanent Products. Upon exposure to ultraviolet light, aqueous solutions of 4-nitrophenylacetate ions rapidly form a precipitate. The yields of products in Table I show a fairly good material balance between the CO_2 yield and the combined nitrobenzyl group yield, even at high per cent decompositions.

The results in Table II indicate that variations in the photolysis conditions have little effect on the quantum yields. Except for strongly acidic solutions the differences are within experimental error, which is high for individual runs due to intensity fluctuations, light scattering by the products, and the analytical accuracy. The carboxyl structure does not show a significant yield of CO_2, and little or no 4-nitrotoluene and 4,4′-dinitrobibenzyl are produced. Similarly, photolysis of 4-nitrophenylacetic acid in nonaqueous solvents (ethanol, acetic acid, pyridine, acetonitrile) does not give appreciable amounts of these photodecarboxylation products. Photodecomposition of strongly acidic aqueous solutions occurs about an order of magnitude slower than that of basic solutions, and different reaction products are formed.

The reaction products and photodecarboxylation efficiency for several nitrophenylacetate ions are compared in Table III. The *m*- and *p*-nitro ions decompose readily, with a quantum yield of approximately 0.6. However, the *o*-nitro compounds react with low efficiency, showing quantum yields of only 0.04. The quantum yields of carbon dioxide are nearly equivalent to the total nitrobenzyl group yield for those ions in which both are measured.

B. Transient Intermediates. Flash photolysis studies reveal the presence of transient species from all of the ions except *m*-nitrophenylacetate ions. These results are summarized in Table IV. The spectra of these transients are obtained by the analysis of many equivalent photolyses as a function of wavelength. In each case the major transient observed is that of an *aci*-nitro structure corresponding to a decarboxylated carbanion residue. The 408-nm absorption maximum from 2-nitrophenylacetate ion photolysis is the same as that of the 2-nitrobenzyl anion transient observed by Wettermark, *et al.*,[15] from the photolysis of 2-nitrotoluene in aqueous base, and from both compounds this intermediate decays at the same rate in 0.1 *N* NaOH. The transient species from 4-nitrophenylacetate ions shifts to a 361 nm maximum in 92 vol % *t*-butyl alcohol, in agreement with the yellow carbanion (4-nitrobenzyl anion) postulated by Russell and Janzen[16] and observed spectrally by Miller and Pobiner[17] from the reaction of *t*-butoxide ions with 4-nitrotoluene in anhydrous *t*-butyl alcohol. Solutions of 4-nitrohomophthalate ions and of 5-nitro-*o*-toluate ions each produce an intermediate with an absorption maximum at 362 nm, and this species fades at the same rate under comparable conditions; the same *aci*-nitro anion (2-carboxylate-4-nitrobenzyl anion) apparently is produced by different photolysis mechanisms.[1] The major transient from the photolysis of 2,4-dinitrophenylacetate ions has the same absorption maximum and decay time as the 2,4-dinitrobenzyl anion observed from the photolysis of 2,4-dinitrotoluene.[18] The photolysis transient from 4,4′-dinitrodiphenylacetate ions has the same absorption

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[12] E. J. Conway, "Microdiffusion Analysis and Volumetric Error," 4th ed, Crosly, Lockwood and Sons, Ltd., London, 1957, p 201.

[13] D. M. W. Anderson, *Talanta*, **2**, 73 (1959).

[14] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

[15] (a) G. Wettermark, *J. Phys. Chem.*, **66**, 2560 (1962); (b) G. Wettermark, E. Black, and L. Dogliotti, *Photochem. Photobiol.*, **4**, 229 (1965).

[16] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

[17] J. M. Miller and H. Pobiner, *Anal. Chem.*, **36**, 238 (1964).

[18] G. Wettermark and R. Ricci, *J. Chem. Phys.*, **39**, 1218 (1963).

Table I. Product Yields from Photolysis of Sodium 4-Nitrophenylacetate

Initial conditions		Photolysis time,^{a} min	% yield^b		
Concn, M	pH		CO_2	4,'4-Dinitrobibenzyl	4-Nitrotoluene
8.0×10^{-2}	10.0	30	31	27	3
3.0×10^{-2}	9.7	30	86	76	5
3.0×10^{-2}	5.3	30	87	71	9
2.3×10^{-2}	8.7	95	95	78	9

^{a} With 200-W Hg arc, stirring solution in closed Pyrex tubes. ^{b} Based on starting material.

Table II. Quantum Yields from 4-Nitrophenylacetic Acid at Various Conditions

Exceptions from normal conditions^a	Φ_{CO_2}	$\Phi_{NB}{}^b$
CO_2 runs at pH 10, not buffered	Av 0.59	Av 0.58
pH 11.8, no buffer, concn, 1.63×10^2 M	0.56	
pH 7.0 buffer		0.56
pH 5.0 buffer	0.47	0.58
pH 4.8, no buffer	0.59	
pH 1.0, HCl, 50% aq ethanol^c	0.00	
pH 1.0, H_2SO_4, 50% aq ethanol	0.00	
Flushed with O_2		0.53
Concn, 5×10^{-3} M		0.52
$I = 1.1 \times 10^{14}$ quanta sec^{-1} cm^2		0.54
λ 313 nm		0.52
λ 313 nm; concn, 5×10^{-3} M		0.48

^{a} Normally 5.0×10^{-2} M in pH 10 borate buffer, N_2 flushed, 367-nm photolysis with ~10^{15} quanta sec^{-1} sec^{-2}. ^{b} Total nitrobenzyl group yield. ^{c} 3-Nitrophenylacetic acid gives the same results.

maximum (515 nm) as that obtained by adding 4 M NaOH to a solution of 4,4'-dinitrodiphenylmethane when comparing solutions of 57 vol % ethanol at −24°. This intermediate is assumed to be the 4,4'-dinitrodiphenyl carbanion.

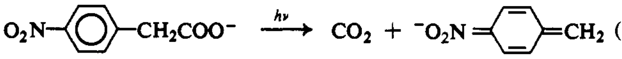
More than one transient species is observed in each nitrophenylacetate ion structure containing an *ortho* substituent. Although not clearly differentiated in the case of 2,4-dinitrophenylacetate ions, these components are resolved in the other *ortho*-substituted compounds. The flash photolysis of 2-nitrophenylacetate ions in the upper pH range shows decay of the transient absorption corresponding to two separate first-order reaction processes. The longer-lived component has the 408-nm peak, as shown in Figure 1 by the upper spectrum. The spectrum of the shorter lived component is calculated by subtracting the back-extrapolated absorption of the longer lived component. Similar results are shown in more detail for 4-nitrohomophthalate ions in Figures 2 and 3. The absorption of the longer lived component in Figure 2 is extrapolated to zero time and subtracted from the initial absorption to obtain the spectrum of the shorter lived component in Figure 3.

The photolysis yields of the major transient species are constant above pH 6 but below this are dependent upon the pH, as shown by the plots of the initial transient absorption in Figures 4 and 5. The yields in Figure 4 from 4-nitrophenylacetic acid and 4-nitrohomophthalic acid follow a straightforward pH dependence. However, a more complex behavior is evident in the curves in Figure 5 from 2-nitrophenylacetic acid.

Since we find the same *aci*-nitro species by photodecarboxylation as occur in photochromic reactions,[1,2,15,18] the relative efficiencies of these two types of reactions are compared in Table V. In each flash photolysis pair, solutions of matched total absorbance absorb approximately equivalent numbers of uv photons.

Discussion

The results are consistent with the general primary process mechanism given in eq 1. Although it is conceivable that the nitrobenzyl anion is formed from a solvated electron which is captured by a nitrobenzyl radical, we have no evidence favoring such a mechanism. In fact, the photodecarboxylation of phenylacetate ions, which have been postulated[7] to occur *via* solvated electron formation, occurs with a quantum yield[2] of only about 0.01 as compared to yields up to 0.6 from the nitrophenylacetate ions. Our mechanism indicates that a material balance should be expected from the CO_2 yield as compared to the total nitrobenzyl group yield in the reaction products. Such a balance is shown by the product yields in Table I and by the quantum yields from the *o*-, *m*-, and *p*-nitrophenylacetate ions in Table III. The material balance in the *para*-compound photolysis is maintained from 1% up to 30% decomposition. The constancy of the quantum yields (Table II) with differences in concentration, light intensity, photolysis wavelength, oxygen concentration, and pH above 5 also provides evidence in favor of a direct photodecarboxylation process. This is shown in reaction 2 as the direct formation


(2)

of the *aci* form of the 4-nitrobenzyl anion. Its reaction with H^+ should produce some 4-nitrotoluene, and the major photolysis product, 4,4'-dinitrobibenzyl, has been produced *via* 4-nitrobenzyl anions by many investigators[16,17,19] from the action of a strong base on 4-nitrotoluene, usually in nonaqueous solvents. The mechanism for the formation of this bibenzyl product is not clear, and it is being investigated in more detail in our laboratory. Although examined only qualitatively, 4,4'-dinitrodiphenylacetate ions photodecarboxylate as readily as the 4-nitrophenylacetate ions, and a red colored *aci*-nitro intermediate is observed.

Our results indicate that the undissociated nitrophenylacetic acids undergo little or no photodecarboxylation in the manner of their carboxylate ions. This lack of reaction is shown by 4-nitrophenylacetic acid in various nonaqueous solvents, in acidified water–ethanol solutions,

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(19) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **89**, 300 (1967), and references cited therein.

Table III. Products and Quantum Yields at 367 nm

Ion	Photolysis products	$\Phi_{CO_2}{}^a$	$\Phi_{NB}{}^b$
2-Nitrophenylacetate	2-Nitrotoluene^c	0.04 ± 0.01	0.05 ± 0.01
3-Nitrophenylacetate	3-Nitrotoluene^c	0.63 ± 0.05	0.52 ± 0.05
4-Nitrophenylacetate	4,4′-Dinitrobibenzyl,^{c} 4-nitrotoluene^d	0.59 ± 0.04	0.58 ± 0.04
4-Nitrohomophthalate	4,4′-Dinitrobibenzyl-2,2′-dicarboxylic acid,^{c} 5-nitro-*o*-toluic acid^d	0.60 ± 0.05	…
2,4-Dinitrophenylacetate	2,4-Dinitrotoluene^c	0.04 ± 0.01	…
4,4′-Dinitrodiphenylacetate	4,4′-Dinitrodiphenylmethane^d	…	…

[a] Unbuffered solution, pH 10, concentration 5.0×10^{-2} *M*, N_2-bubbled. [b] Borate buffer solution, pH 10, concentration 1.0×10^{-2} or 5.0×10^{-2} *M*, total nitrobenzyl group yield. [c] Major product. [d] Formation favored by lower concentration, lower pH, and lower uv intensity.

Table IV. Photolysis Transients from Nitrophenylacetate Ions

Ion	Normal spectrum^a		Photolysis transients^b	
	λ_{max}, nm	$\varepsilon_{max} \times 10^{-4}$	λ_{max}, nm	τ,^{c} sec
2-Nitrophenylacetate	268	0.55	408	0.82
			430	0.015
3-Nitrophenylacetate	273	0.78	…^{d}	…^{d}
4-Nitrophenylacetate	285	0.96	358	53
4-Nitrohomophthalate	285	0.88	362	59
			380	2.6
2,4-Dinitrophenylacetate	253	1.4	530	1.1
4,4′-Dinitrodiphenylacetate	285	2.0	478	71

[a] In NaOH soln, pH 10. [b] Millisecond flash system, concentration $< 4 \times 10^{-5}$ *M*, pH 13 except the last two compds at pH 10 and 12, respectively. [c] Transient lifetime, reciprocal of first-order decay rate constant at 22°, O_2 present. [d] Microsecond flash system: no transient species observed with $\tau > 12$ μsec whose absorption is different from starting material in 320–400-nm range.

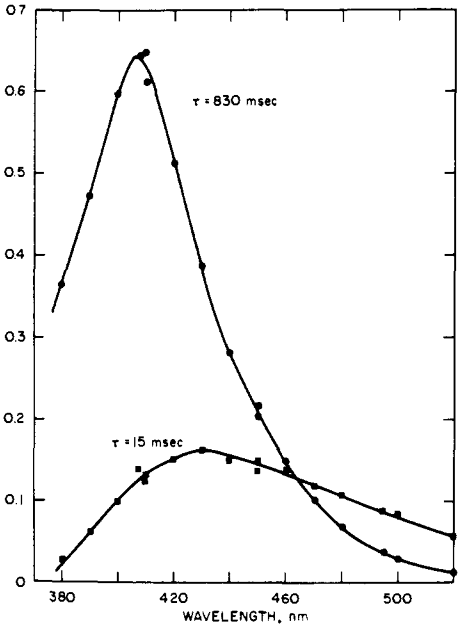


Figure 1. Flash photolysis spectra from sodium 2-nitrophenylacetate, 2×10^{-4} *M*, 5.0-cm cell, pH 12.8, 217 J, 1.8 msec FWHH CS 7-54 filter: ●, longer lived species 100 msec after flash; ■, shorter lived species, calculated 20 msec after flash.

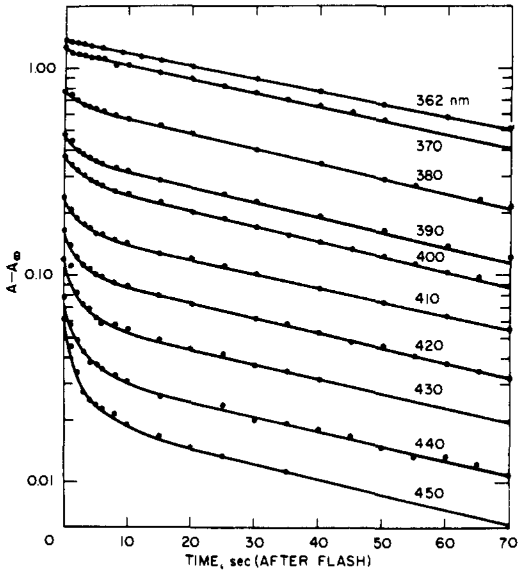


Figure 2. First-order kinetic plots from absorbance decay at various wavelengths after flash of sodium 4-nitrohomophthalate, 2×10^{-5} *M*, pH 13, 5.0-cm cell, 18 J, 150 μsec FWHH, CS 7-54 filter, O_2 present.

and in acidic aqueous solutions. The flash photolysis yield of the *aci*-nitro transient follows a pH dependence in Figure 4 corresponding to the dissociation constant of 4-nitrophenylacetic acid (listed[20] as p*K* = 3.85). The midway breakpoint in Figure 4 gives a p*K* of 3.9 for 4-nitrophenylacetic acid using the following four assumptions: only the carboxylate ion gives the *aci* intermediate; the carboxylic acid and carboxylate ion have approximately equivalent uv integrated absorption coefficients; photolysis does not appreciably alter the pH; and the absorption coefficient of the *aci*-nitro species is constant over the pH range. Our calculated p*K* is slightly higher than the literature value, probably because below pH 3.5 the absorption maximum of the intermediate is shifted to shorter wavelengths due to the formation of the *aci*-nitro

(20) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Co., Cleveland, Ohio, 1967, p D-90.

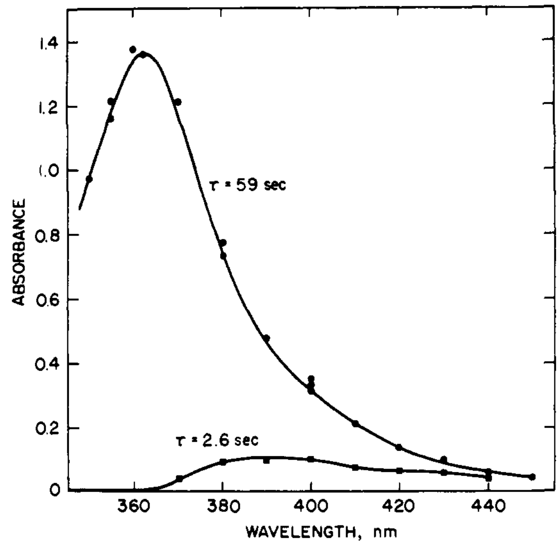


Figure 3. Flash photolysis spectra from sodium 4-nitrohomophthalate, same conditions as in Figure 2: ●, longer lived species 6 sec after flash; ■, shorter lived species, calculated immediately after flash.

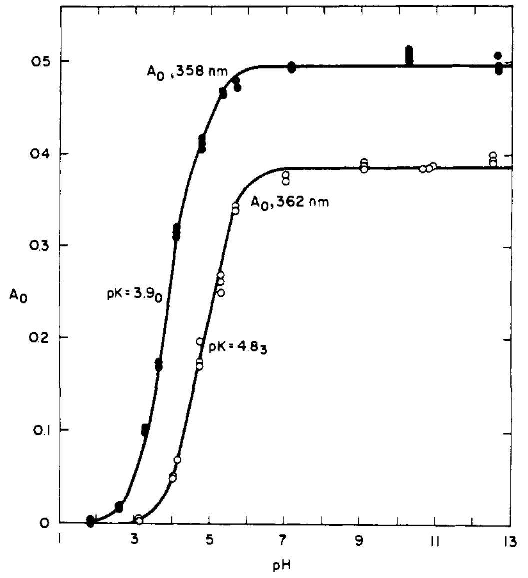


Figure 4. Initial absorbance in flash photolyses, 1.0×10^{-5} *M*, 7.0-cm cell, O_2 present, 10 J, 0.5 μsec FWHH, no flash filter: ●, 4-nitrophenylacetic acid monitored at 358 nm; ○, 4-nitrohomophthalic acid monitored at 362 nm.

acid. Similar effects have been observed in acidic solutions for other *aci* species.[15,18] Below pH 3.5 the apparent absorption coefficient at 358 nm is probably smaller than it is above 3.5 where only *aci*-nitro anion is present.

3-Nitrophenylacetate ions decarboxylate with a high quantum efficiency; however, we find no spectral evidence for a metastable intermediate. This is consistent with the general mechanism since the 3-nitrobenzyl anion would not be resonance stabilized and thus would be expected to behave as a short-lived carbanion. Since the yield of 3-nitrotoluene does not quite balance that of CO_2, there are probably other minor products not identified. The quantum yield of CO_2 is just slightly higher than that from 4-nitrophenylacetate, indicating that the formation of a metastable *aci* anion is not essential for the photodecarboxylation process. On the other hand, the nearly equivalent yields do not fit the mechanisms of Zimmerman[21] in which the excited state of a *m*-nitro structure is considered to be favorable, and that of a *p*-nitro unfavorable, for heterolytic cleavage. Similarly, our decarboxylation results do not follow the photochemical patterns observed by Havinga, *et al.*,[22] in the solvolysis of *m*- and *p*-nitrophenyl phosphates, or of Zimmerman and Somasekhara,[23] in the solvolysis of *m*-

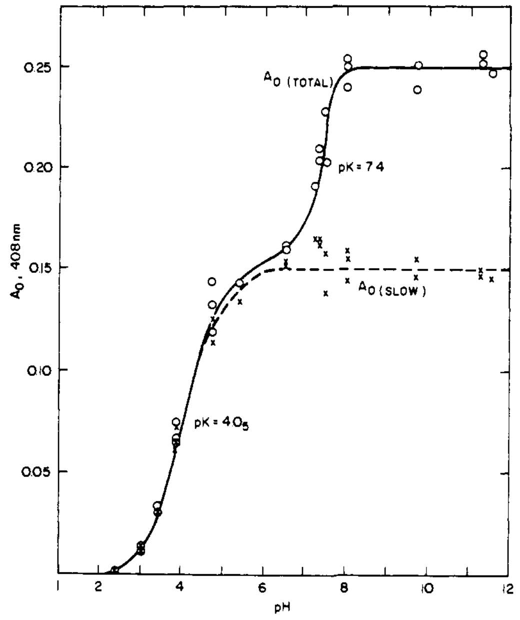
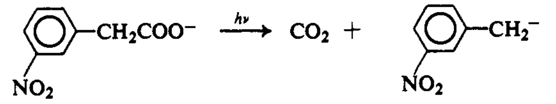


Figure 5. Initial absorbance in flash photolysis of 2-nitrophenylacetic acid, 4.0×10^{-5} *M*, 7.0-cm cell, O_2 present, 25 J, 25 μsec FWHH, CS 7-54, flash filter: ○, total initial absorbance; ×, initial absorbance estimated for longer lived (1 sec) component.

Table V. Estimation of Photochromic Quantum Yields from *aci*-Nitro Transients

Compound or ion	Transient absorption[a] λ_{nm}	Transient absorption[a] A_{aci}	Estimated Φ_{aci}[b]
2-Nitrotoluene[c]	408	0.069	0.01_1
2-Nitrophenylacetate[c]	408	0.289	$[0.04_5]$
2,4-Dinitrotoluene[d]	530	0.056	0.003
2,4-Dinitrophenylacetate[d]	530	0.767	[0.04]
5-Nitro-*o*-toluate[e]	362	0.030	0.06_7
4-Nitrohomophthalate[e]	362	0.271	[0.60]

[a] Solution pairs matched in uv absorption, flashed in 7.0-cm cells, xenon flash lamp with CS 7-54 flash filter. [b] Calculated from the A_{aci} yield and the decarboxylation quantum yield, shown in brackets. [c] Concentration 5×10^{-5} *M*, pH 12.7, A_{aci} read at 100 msec. [d] Concentration 4×10^{-5} *M*, pH 9.8, A_{aci} read at 40 msec. [e] 2×10^{-5} *M*, pH 12.7, A_{aci} read at 4 sec.



(3)

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(21) H. E. Zimmerman, *Advan. Photochem.*, **1**, 203 (1963).

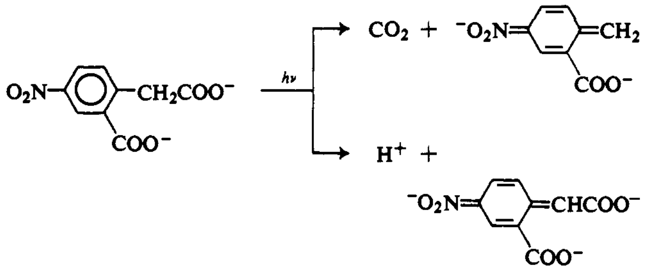
(22) E. O. Havinga, R. O. de Jongh, and W. Dorst, *Rec. Trav. Chim.*, **75**, 378 (1956).

(23) H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **85**, 922 (1963).

and *p*-nitrophenyl trityl ethers. Little or no CO_2 is formed from the photolysis of the 3-nitrophenylacetic acid structure, in agreement with the behavior of the *o*- and *p*-nitrophenylacetic acids.

The 4-nitrohomophthalate ions also decompose efficiently, and the photolysis products are analogous to those obtained from 4-nitrophenylacetate ions. As indicated in Figure 3, two spectral intermediates are observed. The longer lived intermediate (362 nm) corresponds to the decarboxylation reaction 4a, and the shorter lived species (380 nm) is postulated to arise from the photochromic reaction 4b in which hydrogen is transferred internally from the methylene group to the *o*-carboxylate ion and then into the solution. The assignments of these *aci*-anion structures are based on the observation of this same 362-nm intermediate from the photolysis of 5-nitro-*o*-toluate ions,[1] and the observation of a 380-nm band when 40% NaOH is added to solutions of 4-nitrohomophthalate ions in the dark.

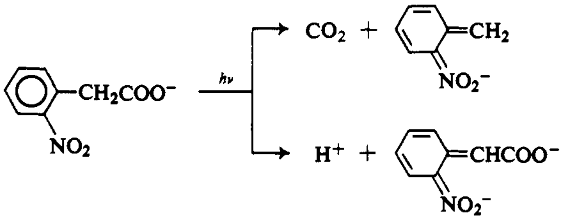
(4a)



(4b)

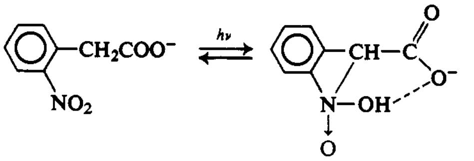
The curve in Figure 4 for 4-nitrohomophthalic acid has a surprisingly simple pH dependence. Since it is a dibasic acid, there are four forms of the parent nitro compounds in this pH range. In addition the dibasic *aci* structure *via* (4a) and the tribasic *aci* structure *via* (4b) could give a total of 12 different *aci*-nitro transients. However, by measuring the absorbance at 362 nm the curve follows the transient from (4a) and minimizes the effect of the minor process (4b). Because *aci*-nitro acids are generally strong acids, the intermediate from (4a) would be expected to exist in only two *aci*-nitro anion forms (carboxyl and carboxylate) above about pH 4.5, and these would not differ much in absorption. Assuming only the phenylacetate structure undergoes photodecarboxylation efficiently, then the curve in Figure 4 indicates that the α-carboxyl group of 4-nitrohomophthalic acid has a p*K* of 4.8.

The effect of structure on the photodecarboxylation reaction is considerable when a nitro group is in the *ortho* position. 2-Nitrophenyl acetate and 2,4-dinitrophenylacetate ions show quantum yields of only 0.04. Kinetic analysis of the spectral intermediates indicates that two different species are present, as shown by the results in Figure 1 where the longer lived species (408 nm) corresponds to the 2-nitrobenzyl anion from photodecarboxylation process 5a, and the shorter lived species (430 nm) is assumed to result from an internal hydrogen-transfer reaction such as (5b). The major reaction product, 2-nitrotoluene, comes from (5a), while (5b) is assumed to be reversible. Figure 5 shows that the yield of the longer lived transient intermediate at 408 nm follows a pH dependence corresponding to decarboxylation from only the carboxylate structure. The midway point for this slow component corresponds within experimental error to the p*K* of 4.0 listed[20] for 2-nitrophenylacetic acid. The fast decay intermediate is observed only above pH 5, and it shows a midpoint break at pH 7.4. This apparent p*K* is much higher than that of the starting compound or the *aci*-nitro structure in (5a), which has been reported[15] to have a p*K* of 3.7. This also seems too high a p*K* for the product of (5b), and an alternative mechanism such as (5b′) may precede (5b); however, considerably more data and analysis will be necessary to resolve this problem.



(5a)

(5b)



(5b′)

Quantum efficiencies for three photochromic hydrogen-transfer reactions are estimated, as shown in Table V, by comparing their yield of *aci*-nitro intermediate with the yield of the same species from photodecarboxylation reactions whose quantum yields are measured independently. The photodecarboxylations are from four to ten times more efficient than the corresponding hydrogen-transfer processes. These results also indicate that in water the photochromic efficiency of *p*-nitrobenzyl compounds containing *o*-carboxylate groups[1] is almost an order of magnitude higher than that of *o*-nitrobenzyl compounds[15,18] studied earlier.

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