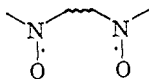


Figure 1. First derivative e.p.r. spectra of: (a) monoradical (IV) and (b) biradical (V) in dimethylformamide. The scale is 5 oersteds for the two spectra. These spectra were recorded on samples which were not degassed. Degassed samples display essentially the same pattern, except for a narrowing of the individual lines.

pendence of the two moieties,^{11a} and bisgalvinoxyl,¹² where no hyperfine structure can be observed in solution. Since structural parameters or solvent effects may change these interactions, further work is now in progress on the synthesis of related biradicals of the general type^{12a}



Acknowledgment. We thank Dr. G. Berthier for suggestions on free radicals and Dr. A. Witkowski for interesting discussions concerning dimers.

(11a) NOTE ADDED IN PROOF. We are indebted to a referee for pointing out that Chichibabin biradical is now known to exist in polymeric form in solution, so that interpretation of its spectrum should be ignored at this stage. See R. K. Waring and G. J. Sloan, *J. Chem. Phys.*, **40**, 772 (1964).

(12) E. A. Chandross, *J. Am. Chem. Soc.*, **86**, 1263 (1964).

(12a) NOTE ADDED IN PROOF. We have now examples of biradicals in which the exchange interaction becomes approximately equal to or significantly less than the hyperfine interaction, according to the distance between the two NO groups. Our results suggest that the interpretations of spectra of biradicals in solution do not necessarily involve explanations such as the so-called "biradical paradox." See H. M. McConnell, *J. Chem. Phys.*, **33**, 1868 (1960).

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Transient Photodecarboxylation Intermediates

Sir:

In the photolysis of aqueous solutions of nitrophenylacetate ions, spectra have been observed which are identified as those of transient photodecarboxylation intermediates. These are probably carbanions which have a strong resonance contribution from their corresponding *aci*-anion structures. The following reaction shown for 4-nitrophenylacetate ions is believed

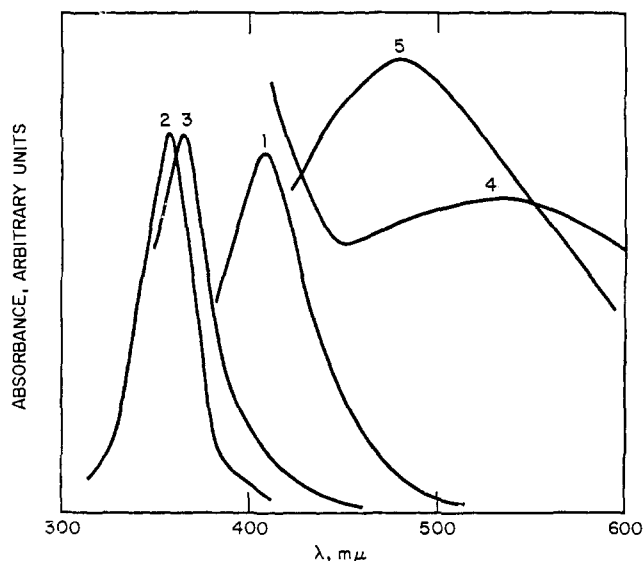
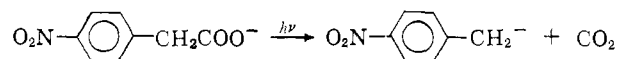
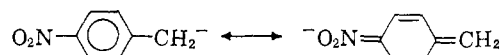


Figure 1. Flash photolysis spectra of photodecarboxylation intermediates (see Table I).

to be typical of the photolyses in which a transient intermediate was observed.



Where



The reaction products and the spectra of the photodecarboxylation transients are shown in Table I and Figure 1.

The transient shown from the flash photolysis of 2-nitrophenylacetate ions had an absorption maximum (408 $m\mu$) and a first-order decay constant (1.0 sec^{-1} in the absence of O_2) identical with those of the *aci*-anion species observed by Wettermark in his photolysis of 2-nitrotoluene.¹ The relative efficiencies for the formation of this species were measured and found to be about three times greater by photodecarboxylation than by the photolytic hydrogen transfer reaction. Nevertheless, the quantum yield of decarboxylation was less than 0.1 at 367 $m\mu$.

No transients with lifetimes longer than 0.5 msec. were found in the photolysis of 3-nitrophenylacetate ions. In contrast to the 2-nitro and 4-nitro compounds, a much weaker contribution to the resonance hybrid would be expected from an *aci*-structure in the 3-nitrobenzyl anion. However, photodecarboxylation occurred readily with a quantum yield of about one-half at 367 $m\mu$.

The intermediate from photolysis of 4-nitrophenylacetate ions had an absorption maximum at 355 $m\mu$ in aqueous base. The maximum shifted to 360 $m\mu$ with *t*-butyl alcohol added up to 92% by volume. The latter position is in close agreement with the spectrum of the carbanion intermediate found by Miller and Pobiner² from the reaction of *t*-butoxide ions on 4-nitrotoluene in *t*-butyl alcohol. Their e.p.r. studies as well as the earlier ones of Russell and Janzen³ showed that this intermediate was not a free radical,

(1) G. Wettermark, *J. Phys. Chem.*, **66**, 2560 (1962).

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

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

Table I. Photodecarboxylations in Aqueous Base

Compd.	Photolysis products isolated ^a	Probable <i>aci</i> type structure	Transient intermediates ^d	
			k_1^e , sec. ⁻¹	Spectrum in Fig. 1
2-Nitrophenylacetic acid	2-Nitrotoluene ^b		1.2	1'
3-Nitrophenylacetic acid	3-Nitrotoluene ^b	
4-Nitrophenylacetic acid	4,4'-Dinitrobibenzyl ^b ; 4-nitrotoluene ^c		0.019	2
4-Nitrohomophthalic acid	5-Nitro- <i>o</i> -toluic acid ^c		0.017	3'
2,4-Dinitrophenylacetic acid	2,4-Dinitrotoluene ^b		0.90	4 ^o
4,4'-Dinitrodiphenylacetic acid	4,4'-Dinitrodiphenylmethane ^c		0.014	5

^a In addition to CO₂, identified as carbonate. ^b Major product from 10⁻² M solution. ^c Product favored by low concentration, low pH, and low ultraviolet intensity. ^d From flash photolyses: concentration < 4 × 10⁻⁸ M; pH 13, except spectra 4 and 5 at pH 10 and 12, respectively. ^e Approximate first-order decay rate constant at 22° in presence of oxygen. / The longer lived of two transients. ^o The shorter lived of two transients.

and that it probably dimerized to a bibenzyl structure prior to any free radical formation. In both of their studies and in the photodecarboxylation, 4,4'-dinitrobibenzyl was found as the major reaction product. However, no red-colored species, corresponding to the radical anions eventually formed from *t*-butoxide on 4-nitrotoluene, were found in the aqueous photolyses of 4-nitrophenylacetate ions. The photodecarboxylation products readily precipitated out of solution and were formed with a quantum yield of about 0.6 at 367 mμ for the 4,4'-dinitrobibenzyl and 4-nitrotoluene combined. Longer periods of photolysis gave up to 90% decomposition of the starting material. Carbon dioxide was found in equivalent amounts to the total 4-nitrobenzyl group content of the products. Undissociated 4-nitrophenylacetic acid in various solvents (ethanol, ethanol-6 N HCl, acetonitrile, pyridine, etc.) did not undergo appreciable photodecarboxylation. In aqueous solutions the final products isolated were essentially the same in the presence or absence of oxygen.

The spectrum shown for the transient intermediate from the decarboxylation of 4-nitrohomophthalate ions was found to be in good agreement with an intermediate (λ_{\max} at 362 mμ) from the photolysis of 5-nitro-*o*-toluate ions.⁴ Presumably the same *aci*-anion was formed from both compounds: by loss of CO₂ in the former case, and by proton transfer in the latter case. This *aci*-anion was formed about three times more efficiently by photodecarboxylation than by the hydrogen transfer photolysis.

The spectrum and decay rate of the decarboxylation intermediate from the photolysis of 2,4-dinitrophenylacetate ions were similar to those of the *aci*-anion reported by Wettermark and Ricci in the flash photolysis of 2,4-dinitrotoluene.⁵ The observed intermediate was found to be formed six times more readily by photodecarboxylation of the dinitrophenylacetate ion than by photolytic hydrogen transfer in dinitrotoluene. The red transient from photolysis of 4,4'-dinitrodi-

phenylacetate ions was easily observed visually. In more concentrated aqueous solutions the products precipitated out of solution as the red color faded. At -24° in dilute base containing 57% ethanol, the absorption maximum of the photolysis intermediate shifted up to 515 mμ. This was in agreement with the spectrum found by the addition of excess 4 M NaOH to a similar solution of 4,4'-dinitrodiphenylmethane.

Two transients were observed for the three compounds with *ortho* substituents. In each case another species (not shown here) was formed, presumably by a competing proton transfer photolysis reaction in which an *aci* structure was formed without the loss of carbon dioxide.^{4,6} The competing phototropic reactions reduced the efficiency of the photodecarboxylation reaction as compared to that of the other compounds without an *ortho* substituent.

The presence of an aromatic nitro group greatly enhanced photolytic decarboxylation. Phenylacetic acid (un-nitrated) in aqueous base showed only slight photodecarboxylation. At 250 mμ, CO₂ from photolysis of phenylacetate ions was formed at only 1.5% of the efficiency with which it was formed from 4-nitrophenylacetate ions.

It is interesting to note that in contrast to what might have been expected from Zimmerman's excited state mechanistic pictures,⁷ the 4-nitrophenylacetate structure underwent this heterolytic photodecarboxylation reaction as readily as the 3-nitrophenylacetate structure.

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(7) W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., *Advan. Photochem.*, **1**, 203 (1963).

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