

Photoreactions of Polycyclic Aromatic Hydrocarbons with *N*-Arylglycines

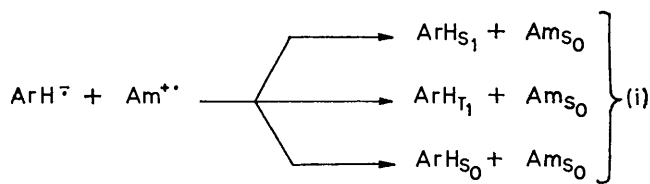
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Irradiation of aerated solutions of polycyclic aromatic hydrocarbons in acetonitrile containing *N*-arylglycines leads to decarboxylation of the acids. Other products include anilines and formanilides. The reaction occurs less readily in benzene solution. Since the amino-acids quench the fluorescence of the hydrocarbons at nearly the diffusion-controlled limit, the reaction is thought to occur from the first excited singlet state of the hydrocarbon. The primary photochemical process is ascribed as the transfer of an electron from the amino-acid to the excited hydrocarbon. The relevance of this electron-transfer reaction to those undergone by triplet excited states is discussed.

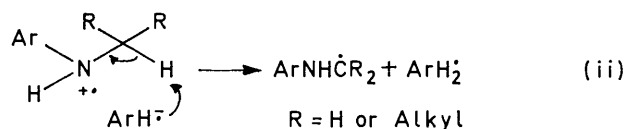
WELLER¹ and others² have previously shown that the first excited singlet state of many polycyclic aromatic hydrocarbons undergoes an electron-transfer reaction with amines. In non-polar solvents exciplex intermediates, *i.e.* intermediates formed by partial electron transfer from the amine to the excited hydrocarbon, can be observed. In highly polar solvents the electron transfer goes to completion, and radical ion formation has been observed by the techniques of microsecond^{1b} and nanosecond³ flash photolysis. It was found that under conditions which favour radical ion formation, reduction of the aromatic hydrocarbon occurred, whereas in contrast little chemical reaction took place under conditions which favoured exciplex formation.⁴ The intermediacy of radical ions has been shown by deuterium-labelling studies.⁵ More recently, Bryce-Smith and his co-workers have demonstrated the catalytic effect of protic solvents upon the reduction of benzenoid compounds by amines, and this can easily be rationalised in terms of radical ion intermediates.⁶

The radical ions produced by electron transfer can undergo a quenching reaction by back transfer of the electron [equation (i)] or proceed to give radicals by the transference of a proton [equation (ii)]. In oxygenated solution, the hydrocarbon radical can react with oxygen resulting in regeneration of the hydrocarbon whereas the amine radical reacts with oxygen to give a variety of oxidation products.⁷ When oxygen is absent the hydrocarbon and amine radicals may combine, disproportionate, or undergo dimerisation reactions. The efficiency of the reaction which leads to radical formation [equation (ii)] will depend on the efficiency of the back electron

transfer reaction [equation (i)] and on the ease of the proton transfer. Thus, increasing the acidity of a

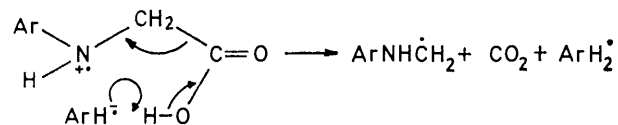


ArH = Aromatic hydrocarbon Am = Amine



SCHEME 1

proton available for transfer to the aromatic hydrocarbon radical anion should favour the reaction. For this reason the photoreactions of excited polycyclic aromatic hydrocarbons with *N*-arylglycines were investigated. Besides the acidity of the carboxylic acid



SCHEME 2

hydrogen favouring reaction, there is the added bonus that a stable molecule, carbon dioxide, is being formed.

¹ R. Potashnik, C. R. Goldschmidt, M. Ottolenghi, and A. Weller, 6th International Conference on Photochemistry, Bordeaux, September 1971.

² R. S. Davidson, *Chem. Comm.*, 1969, 1450.

³ C. Pac and H. Sakurai, *Tetrahedron Letters*, 1969, 3829.

⁴ D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Comm.*, 1971, 916.

⁵ R. F. Bartholomew and R. S. Davidson, *J. Chem. Soc. (C)*, 1971, 3482.

¹ (a) D. H. Rehm and A. Weller, *Israel J. Chem.*, 1970, **8**, 259, and references cited therein; (b) H. Leonhardt and A. Weller, *Z. phys. Chem. (Frankfurt)*, 1961, **29**, 277.

² A. Nakajima, *Bull. Chem. Soc. Japan*, 1969, **42**, 3409; N. Mataga, J. Okada, and H. Oohari, *ibid.*, 1966, **39**, 2563; M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, 1969, **3**, 71; R. J. McDonald and B. K. Selinger, *Austral. J. Chem.*, 1971, **24**, 1797.

RESULTS

Irradiation of solutions of polycyclic aromatic hydrocarbons in acetonitrile containing *N*-arylgylicines was found to lead to decarboxylation. In the absence of oxygen a complex reaction mixture was obtained. For example, reactions of anthracene and phenanthrene with *N*-phenylglycine gave aniline, *N*-methylaniline, and the

DISCUSSION

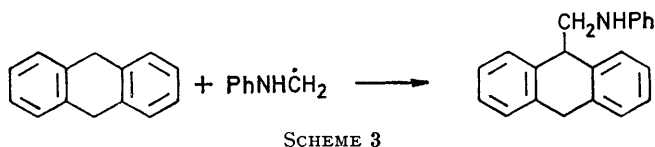
Table 1 shows that a variety of polycyclic aromatic hydrocarbons are able to bring about decarboxylation of *N*-arylgylicines, although there are two examples in which reaction did not occur. An unequivocal explanation for these failures cannot be given at present but it is suggested that the back electron transfer reaction

TABLE 1
Products formed by irradiation of oxygenated solutions of polycyclic aromatic hydrocarbons in acetonitrile containing *N*-arylgylicines

Hydrocarbon	<i>N</i> -Phenylglycine			<i>N</i> -(<i>o</i> -Chlorophenyl)glycine			<i>N</i> -Methyl- <i>N</i> -phenylglycine		
	CO ₂ yield (%)	Aniline ^a (%)	Formanilide ^a (%)	CO ₂ yield (%)	<i>o</i> -Chloro-aniline (%)	<i>o</i> -Chloro-formanilide (%)	CO ₂ (%)	<i>N</i> -Methyl-aniline ^a (%)	<i>N</i> -Methyl-formanilide ^a (%)
Anthracene	75	42	33	75	43	32	68	27	46
Phenanthrene	72	40	30	40	41	31	77	39	36
Benz[<i>a</i>]anthracene	77	40	41	88	42	35	68	31	48
Naphthalene	58	45	40	No detectable reaction			46	31	39
Perylene	63	32	39	No detectable reaction			69	41	44

^a Yield based on amount of acid decarboxylated.

corresponding dihydro-derivative of the hydrocarbon as well as unidentified material. The yield of the characterised compounds was low; the main product or products was not identified. I.r. and mass spectral data for this material suggested that it was derived by combination of the aminomethyl radical and the hydrocarbon radical (Scheme 3). In order to suppress this reaction,



with the hope that the amount of identifiable material would be increased, the reactions were run in the presence of oxygen. This hope was realised, and products and yields are shown in Table 1. In all cases, little of the aromatic hydrocarbon was consumed in the reactions. Decarboxylation occurred much more slowly in benzene solution than in acetonitrile solution (see Table 2). *N*-Arylgylicines quench the fluorescence of aromatic hydrocarbons and a quantitative study was made of this process. The rate constants for the quenching reactions are shown in Table 3.

TABLE 2

Yields (%) of carbon dioxide from the photoreaction^a of aromatic hydrocarbons with *N*-phenylglycine and *N*-methyl-*N*-phenylglycine in deoxygenated benzene and acetonitrile solutions

Hydrocarbon	<i>N</i> -Phenylglycine		<i>N</i> -Methyl- <i>N</i> -phenylglycine	
	Benzene	Acetonitrile	Benzene	Acetonitrile
Anthracene	11	43	15	69
Phenanthrene	15	76	21	95
Naphthalene	12	58	15	81
Benz[<i>a</i>]anthracene	13	70	16	87
Perylene	20	47	23	76

^a All irradiations carried out under similar conditions and for the same length of time.

[equation (i)] may be much more efficient than the proton transfer step [equation (ii)].

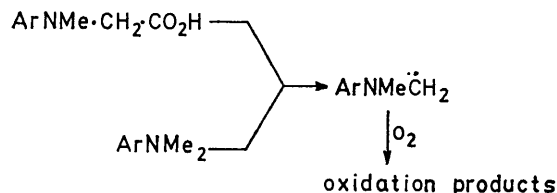
The products derived by oxidation of *N*-methyl-*N*-phenylglycine are the same as those derived by oxidation

TABLE 3

Rate constants for the quenching of fluorescence of aromatic hydrocarbons by *N*-arylgylicines in acetonitrile solution

Hydrocarbon	<i>N</i> -Phenylglycine ($k/\text{mol}^{-1} \text{s}^{-1}$)	<i>N</i> -Methyl- <i>N</i> -phenylglycine ($k/\text{mol}^{-1} \text{s}^{-1}$)
Anthracene	1.4×10^{10}	2.1×10^{10}
Benz[<i>a</i>]anthracene	8.6×10^9	1.0×10^{10}
Perylene	1.2×10^{10}	1.9×10^{10}
Phenanthrene	9.2×10^9	1.1×10^{10}

of *NN*-dimethylaniline sensitised by benzophenone.⁸ This is to be expected since the same aminomethyl radical is involved in both reactions.

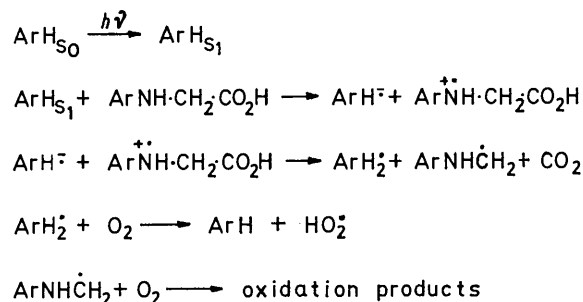


The first excited singlet state of the aromatic hydrocarbons appears to be the excited state responsible for reaction. This follows from the observation that the amino-acids quench the fluorescence of the aromatic hydrocarbons very efficiently and from the fact that the reactants were used in concentrations at which most of the fluorescence of the hydrocarbon was quenched. Furthermore, the finding that the reaction occurs much more readily in acetonitrile than in benzene solution, suggests that the reaction occurs by an electron-transfer

⁸ R. F. Bartholomew and R. S. Davidson, *Chem. Comm.*, 1970, 1174; *J. Chem. Soc. (C)*, 1971, 2342.

process. From the results obtained in the reactions of tertiary amines with aromatic hydrocarbons⁴ one might have anticipated that the decarboxylation reaction would not occur in benzene solution. However, the greater acidity of the hydrogen atom of the carboxy-group compared with the hydrogen attached to the α -carbon atom of amines will favour the proton transfer step and thus reaction may therefore be occurring within the exciplex. A similar situation occurs with secondary amines, which have ionisation potentials low enough to react with the aromatic hydrocarbons. With these compounds, *e.g.* pyrrole,⁹ reaction occurs just as readily in acetonitrile as in benzene.

From the quenching data and the solvent effect we conclude that the reactions of aromatic hydrocarbons with arylglycines involve the first excited singlet state of the hydrocarbon, which undergoes an electron transfer reaction with the amino-acid.



SCHEME 5

There has been much recent speculation and evidence¹⁰ concerning the participation of excited triplet states in electron-transfer reactions. The finding that the first excited singlet state of polycyclic aromatic hydrocarbons sensitises the decarboxylation of *N*-arylglycines forms an important bridge between the triplet^{10b} and singlet-sensitised electron transfer reactions. In principle, if we have an excited species X, which undergoes an electron-transfer reaction with species Y to give radical



SCHEME 6

ions, then the resulting chemical reaction between the radical ions should be independent of the multiplicity of the excited species X. Several triplet states, *e.g.* those derived from carbonyl compounds, nitro-compounds, and some dyes, sensitise the decarboxylation of *N*-arylglycines, as does the first excited singlet state of the aromatic hydrocarbons. This similarity in behaviour provides one more piece of strong evidence for the occurrence of electron-transfer processes in reactions of excited triplet states.

EXPERIMENTAL

Reagents.—Benzene (AnalaR) was dried over sodium wire and distilled from calcium hydride as required.

⁹ J. J. McCullough and W. S. Wu, *Tetrahedron Letters*, 1971, 3951; J. J. McCullough, W. S. Wu, and C. W. Huang, *J.C.S. Perkin II*, 1972, 370.

Acetonitrile (Koch–Light Puriss grade) was distilled prior to use. Naphthalene ('reagent' grade) and anthracene ('blue-fluorescence' grade) were used as received from B.D.H. Phenanthrene ('reagent' grade, B.D.H.) was found to contain anthracene. This impurity was removed by irradiation of a degassed solution of the crude phenanthrene in benzene. The photodimer of the anthracene, produced in this way was easily removed by recrystallisation. Perylene and benz[*a*]anthracene were used as received from R. N. Emanuel Ltd.

Spectra and G.l.c. Analysis.—I.r. spectra for samples in Nujol or as thin films were obtained with a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained with an A.E.I. MS9 instrument. Only the value for the molecular ion is given. G.l.c. analysis was carried out with a Pye–Umicam series 104 chromatograph equipped with a flame ionisation detector. The detector gave a linear response over the whole range of concentrations used. Products were identified by a comparison of their retention times with those of authentic materials. Quantitative estimation was carried out by comparison of peak areas with those from authentic samples. More than one determination was always carried out and reproducibility was within 5%. Aniline, *o*-chloroaniline, and *N*-methylaniline were determined by use of a glass column (5 ft \times 1/4 in) containing 10% Apiezon L on 100–120 mesh acid-washed Diatomite C at 130, 140, and 160°, respectively. Formanilide, *o*-chloroformanilide and *N*-methylformanilide were determined by use of a column containing 3% OV 17 on silanised 100–120 mesh Diatomite C.

Determination of the Yields of Carbon Dioxide.—The carbon dioxide was determined as barium carbonate by the previously recorded procedure.^{10b}

Irradiation Procedure for Decarboxylation Reactions run in the Presence of Oxygen.—The reaction mixture [in acetonitrile (25 ml)], contained in a Quartz tube (1 cm diam.) was continuously purged with dry carbon dioxide-free oxygen. The exit gases were passed through saturated solutions of barium hydroxide. In all cases the reaction solutions were $1 \times 10^{-3}\text{M}$ in sensitiser and $5 \times 10^{-2}\text{M}$ in amino-acid. After 15 min flushing by the gas the sample was irradiated with a Rayonet Photochemical Reactor. When benz[*a*]anthracene and anthracene were used as sensitisers, lamps having maximum emission at 350 nm were used. For phenanthrene and naphthalene, lamps having maximum emission at 310 nm were used. When perylene was used, the sample was irradiated with $8 \times 25\text{ W}$ 'Daylight' Mazda fluorescent lamps, which were arranged in a circle around the sample. After irradiation the mixture was flushed with pure oxygen for a further 15 min in order to displace all the carbon dioxide present. The products and their yields were determined by g.l.c. analysis.

Comparison of the Rates of Formation of Carbon Dioxide in Decarboxylation Reactions in which Benzene and Acetonitrile were used as Solvents.—A solution of the sensitiser ($5 \times 10^{-2}\text{M}$) and amino-acid ($5 \times 10^{-2}\text{M}$) in either acetonitrile or

¹⁰ (a) J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, 1972, **94**, 4040, and references cited therein; P. J. Wagner and A. E. Kemppainen, *ibid.*, 1971, **93**, 7002; A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *ibid.*, p. 6998, and references cited therein; R. F. Bartholomew, R. S. Davidson, P. F. Lambeth, J. F. McKellar, and P. H. Turner, *J.C.S. Perkin II*, 1972, 577; (b) R. S. Davidson and P. R. Steiner, *Chem. Comm.*, 1971, 1115; *J. Chem. Soc. (C)*, 1971, 1682; *J.C.S. Perkin II*, 1972, 1357; R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc. (C)*, 1971, 3480; R. S. Davidson, S. Korkut, and P. R. Steiner, *Chem. Comm.*, 1971, 1052.

benzene (150 ml) was irradiated with a 100 W Hanovia medium-pressure mercury arc housed in a Pyrex water-cooled well. The mixture was continuously purged with carbon dioxide-free nitrogen and the exit gases were passed through barium hydroxide solutions. From the amount of barium carbonate precipitated the amount of carbon dioxide formed was calculated. In all cases irradiations were carried out for 3 h.

Decarboxylation of N-Phenylglycine in Acetonitrile Solution Sensitised by Anthracene.—A solution of anthracene (1.0 g) and *N*-phenylglycine (1.0 g) in acetonitrile (150 ml) was irradiated with a 100 W Hanovia medium-pressure mercury lamp contained in a water-cooled Pyrex well. Throughout the 15 h irradiation the mixture was continuously purged with nitrogen. G.l.c. showed that *N*-methylaniline (0.15 g, 22%) and aniline (0.04 g, 5%) were formed. During the irradiation 9,9',10,10'-tetrahydro-9,9'-bianthryl (0.31 g, 31%) crystallised out, m.p. and mixed m.p. 240—243° (from benzene). The solvent was removed from the mixture and the residue chromatographed on alumina (100 g). Elution with light petroleum (b.p. 40—60°) gave 9,10-dihydranthracene (0.12 g, 12%), m.p. and mixed m.p. 107—108°, and anthracene (0.15 g), m.p. and mixed m.p.

216°. Elution with benzene gave a dark red oil (0.43 g), ν_{\max} 725 and 777 cm^{-1} (1,2-disubstituted benzene), m/e 385. Attempts to purify and characterise this material were unsuccessful.

Decarboxylation of N-Phenylglycine in Acetonitrile Solution Sensitised by Phenanthrene.—A solution of phenanthrene (1.0 g) and *N*-phenylglycine (1.0 g) in acetonitrile (150 ml) was irradiated under conditions similar to those used in the previous experiment. After 15 h the reaction mixture was analysed by g.l.c. *N*-Methylaniline (0.15 g, 22%) and aniline (0.11 g, 16%) were found. The solvent was removed and the residue chromatographed on alumina (100 g). Elution with light petroleum gave 9,10-dihydrophenanthrene (0.16 g, 15%), m.p. and mixed m.p. 33—34°, and phenanthrene (0.18 g), m.p. and mixed m.p. 99—100°. Elution with benzene gave a red oil (0.54 g), ν_{\max} 740 and 810 cm^{-1} (1,2-disubstituted benzene), m/e 385. Further attempts to purify and characterise this material were unsuccessful.

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