effect ($k_{\mathrm{cat}}^{\mathrm{H_2O}}/k_{\mathrm{cat}}^{\mathrm{D_2O}} = 1.1 \pm 0.1$ at pH 4.0) consistent with nucleophilic catalysis. This result also excludes general acid catalysis by the protonated imidazolyl group of the single histidine residue in pepsin. Since Clement and Snyder[16] have also reported the absence of a deuterium solvent kinetic isotope effect in the hydrolysis of a peptide substrate, it appears that the absence of general acid-base catalysis is the most distinctive feature of pepsin-catalyzed hydrolyses.

Ted W. Reid, David Fahrney
Department of Chemistry, University of California
Los Angeles, California 90024

Received April 24, 1967

Photochemistry of Aromatic Ions. Photolysis of Quaternary Anilinium Salts

Sir:

No direct evidence has been reported concerning the process preceding dissociation in the photolysis of substituted benzenes, although several derivatives have been studied in detail to show that phenyl radicals are produced.[1,2] In particular, ionic derivatives require some type of charge transfer in the production of these radicals.[1a,b] Three distinctly different paths leading to phenyl radicals are outlined for ArX^+Y^-. Path A

$$\mathrm{ArX^+} \xrightarrow{h\nu} [\mathrm{ArX^+}]^* \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}\cdot^+ \qquad \text{(A)}$$

$$\begin{array}{c} \mathrm{Y^-} \longrightarrow [\mathrm{Y^-}]^* \xrightarrow{h\nu} \mathrm{Y}\cdot + \mathrm{e^-(solv)} \\ \mathrm{e^-(solv)} + \mathrm{ArX^+} \longrightarrow [\mathrm{ArX}] \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}\cdot \end{array} \qquad \text{(B)}$$

$$\mathrm{ArX^+Y^-} \xrightarrow{h\nu} [\mathrm{ArX,Y}]^* \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}\cdot + \mathrm{Y}\cdot \qquad \text{(C)}$$

predicts no effect of changing anion and corresponds to the process generally cited for photolyses of nonionic materials.[1c] Path B has ample precedent in the literature concerned with generation and reactions of solvated electrons.[3] Path C involves direct charge transfer, requiring counterion proximity and suitable interaction.

Aryltrimethylammonium salts, $p\text{-RC}_6\text{H}_4\text{N(CH}_3)_3{}^+\text{Y}^-$ (I), have been studied. The positively charged nitrogen atom exerts only an inductive effect on the ring, yet such compounds are known to be readily reduced electrolytically[4] or by alkali metals.[5] Their photochemical behavior has not been reported.

Oxygen-free 1% methanolic solutions of I readily yield the corresponding hydrocarbon and trimethylamine upon irradiation.[6] Ethyl and isopropyl alcohols are also suitable, each yielding the corresponding aldehyde or ketone. Water and *t*-butyl alcohol are unsatisfactory. Formation of phenyl radicals is further confirmed by the complete absence of anisole among the products and observation of ethylene glycol at higher substrate concentrations.

Absorption of light by the aromatic ring appears to be necessary. Cyclohexyltrimethylammonium iodide was recovered unchanged after 17 hr. Irradiation of I (R = H, Y = C_6H_5O) in Pyrex for several days resulted in decomposition of the phenoxide ion, but no benzene was detected. In contrast, irradiation in quartz afforded a 51% yield after 6 hr. Removal of the nitrogen from direct attachment to the aromatic ring hinders the reaction; benzyltrimethylammonium iodide yields only 10% toluene after 14 hr.

A series of anions was investigated, and the results are shown in Table I. The percentage of recovered starting material was obtained in most cases by vapor phase chromatography; the salts decompose readily in the inlet to yield the corresponding dimethylaniline.[7] The uniformly high material balance indicates that the figures in the table are a valid although approximate reflection of the relative reactivities, which clearly vary markedly. Effective anions are those which are known to be easily photooxidized.[8] Path A must therefore be discarded.

Table I. Irradiation of $p\text{-RC}_6\text{H}_4\text{N(CH}_3)_3{}^+\text{Y}^-$ for 2 Hr in Methanol

R	Y	% ArH	% recovered[a]
H	I	61	28
H	$C_6H_5CO_2$	51	40
H	C_6H_5O[b]	50	
H	$C_6H_5CH_2CO_2$	14[c]	63
H	AcO	4	71
H	Cl	0	*d*
H	CHO_2	0	85
H	BF_4	0	80[e]
CH_3O	I	90	<1
CH_3	I	78	16
F	I	71	25
CH_3O_2C	I	0	
CN	I	0	>90[e]

[a] By vpc (see text). [b] Irradiation time 6 hr. [c] Plus 14% toluene. Yields were 55 and 69% after 14 hr. [d] Addition of 1 equiv of NaI resulted in a 60% yield of benzene after 4 hr further irradiation. [e] Isolated.

Results obtained with various *para*-substituted derivatives (Y = I) illustrate the fact that electron-donating substituents favor the reaction whereas the yield drops drastically with electron-withdrawing groups. This speaks strongly against path B, if one assumes that reactivity is proportional to electron-scavenging ability. Anbar and Hart found $\rho = +4.8$ for the reaction between aromatic molecules and hydrated electrons.[9] In addition, the efficacy of phenoxide ion in promoting the photolysis eliminates path B. Although phenoxide is an excellent hydrated electron source,[8a] such a process is not detectable in methanol, while phenoxy radical

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[1] (a) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Am. Chem. Soc.*, **83**, 1928 (1961); (b) C. E. Griffin and M. L. Kaufman, *Tetrahedron Letters*, 773 (1965); (c) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965); (d) N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

[2] G. A. Razuvaev and Yu A. Ol'dekop, *Zh. Obshch. Khim.*, **19**, 736 (1949), and references cited therein.

[3] E. J. Hart, Symposium Chairman, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965.

[4] (a) B. Emmert, *Chem. Ber.*, **42**, 1507 (1909); (b) V. Gutmann, G. Schöber, and K. Utvary, *Monatsh.*, **88**, 887 (1957); (c) L. Horner and A. Mentrup, *Ann. Chem.*, **646**, 49 (1961); (d) M. Finkelstein, R. C. Petersen, and S. D. Ross, *Electrochim. Acta*, **10**, 465 (1965).

[5] A. J. Birch, *J. Proc. Roy. Soc., N. S. Wales*, **83**, 245 (1949).

[6] Irradiations were conducted using a bank of ten GE G25-T8 germicidal lamps with approximately 96% output at 2537 A. All analyses were performed by vapor phase chromatography, using Porapak Q solid substrate (Waters Associates, Inc.). Yields were calculated by comparison of peak area with a calibrated standard for each compound.

[7] A. D. Site, *J. Org. Chem.*, **31**, 3413 (1966).

[8] (a) G. Stein, ref 3, p 230; (b) L. I. Grossweiner and H.-I. Joschek, ref 3, p 279.

[9] M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).

production is apparently unaffected.[8b,10] Aromatic anions in general are poor solvated electron sources in alcohols,[8b] but several are acceptable in the present case.

All the evidence is in accord with a direct charge-transfer excitation of associated ions (path C). Conductivity studies[4b,11] and vapor pressure measurements show that these salts are appreciably associated at the concentrations employed. Further evidence was obtained by observation of a charge-transfer band at 290 mμ (log ϵ 2.94) for I (R = CN, Y = I) in 10% $CH_3OH-CHCl_3$. This band is absent in the fluoroborate and in more polar solvents, as expected.[12] Addition of solid KI to a solution of the fluoroborate results in gradual formation of the 290-mμ band.

The pronounced effect of ring substituents is readily understood within this framework. Only when the energy of the charge-transfer state is sufficiently high to allow crossover into the dissociative state will reaction occur. Electron-attracting groups have little effect on the energies of the ground and dissociative states, but can greatly stabilize the charge-transfer state through conjugation.

The interionic charge transfer demonstrated here is not necessarily demanded by other charged benzene derivatives. In fact, benzenediazonium fluoroborate photolyzes smoothly under our conditions to yield 51% benzene after 2 hr, possibly through intervention of N_2^+.

(10) L. I. Grossweiner, E. F. Zwicker, and G. W. Swenson, *Science*, **141**, 1042 (1963).

(11) P. G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Chem. Phys.*, **23**, 1274 (1955).

(12) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

(13) To whom correspondence should be sent: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

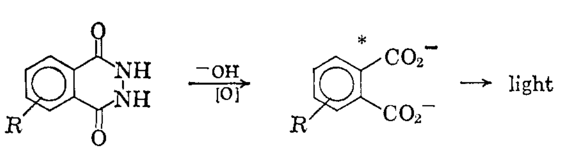
Thomas D. Walsh,[13] Robert C. Long
Department of Chemistry, University of Georgia
Athens, Georgia 30601

Received May 10, 1967

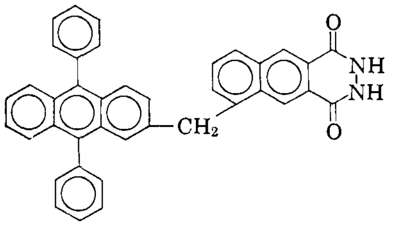
Intramolecular Energy Transfer in Chemiluminescence

Sir:

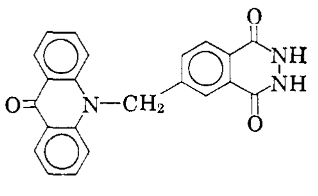
We wish to report a type of chemiluminescence that involves intramolecular energy transfer. In the chemiluminescence of luminol and related hydrazides (I), the product, the dicarboxylate ion II, is formed in an excited singlet state; emission of a photon then completes the process.[1-3] The direct relationship of the fluorescence quantum yield of II and the quantum yield of I in chemiluminescence has been noted.[1] Thus, for efficient light production, highly fluorescent compounds are required. This simple approach is usually not completely successful, however, because the conjugated systems needed to achieve a high fluorescence efficiency are readily destroyed by the oxidizing agents used; furthermore, the larger systems have absorption bands in the visible region, and self-quenching becomes an important problem. To circumvent these difficulties, we have separated the energy-generating and light-emitting functions (compounds III and IV). The expectation was that intramolecular energy transfer would occur from the hydrazide portion to the fluorescent portion. Energy transfer has been shown to occur in difunctional molecules A–B where the donor A was raised to an excited state by light absorption and emission occurred from moiety B;[4] in the present case, chemical energy is used to reach the excited state of the donor. The use of chemical energy is advantageous since it ensures that all the energy is originally located in the donor.



I II

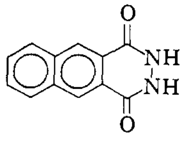


III

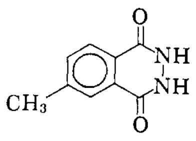


IV

The energy levels for transfer are satisfactory for compounds III and IV, since naphthalic hydrazide (V) emits at 355 mμ in the aqueous system (the fluorescence of the naphthalenedicarboxylate ion is at the same wavelength), whereas diphenylanthracene shows absorption bands out to 405 mμ. Similarly, acridone shows absorption out to 400 mμ and, although the exact value is unknown, it is certain that the excited singlet energy of phthalate ion is higher than that of the naphthalenedicarboxylate ion.



V



VI

Compounds III and IV were tested in an aqueous system ($H_2O-NaOH-H_2O_2$, hemin) and also in the dimethyl sulfoxide system (DMSO + H_2O (9:1)–$NaOH-O_2$). The data indicate (Table I) that intra-

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(1) E. H. White, O. C. Zafiriou, H. H. Kagi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964).

(2) K. D. Gundermann, *Angew. Chem.*, 77, 572 (1965); Symposium on Chemiluminescence, Durham, N. C., 1965 (Army Research Office, Durham).

(3) The general mechanism proposed by A. U. Khan and M. Kasha (*J. Am. Chem. Soc.*, **88**, 1574 (1966)) cannot be operating in the chemiluminescence of the hydrazides (and the lophines: E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965)) since the critical energy-producing reactions consume, but do not produce, oxygen. See also F. McCapra, *Quart. Rev.* (London), **20**, 485 (1966), and M. M. Rauhut, B. G. Roberts, and A. M. Semsel, *J. Am. Chem. Soc.*, **88**, 3604 (1966).

(4) A. A. Lamola, P. A. Leermakers, G. W. Byers, and G. S. Hammond, *ibid.*, **87**, 2322 (1965); S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965).