dediazoniation of diazonium tetrahalogenoborates, as simple halide counterions (Cl^- and Br^-) seem to favor a decomposition of the diazonium compound via a radical mechanism. A possible explanation for this observation can be based on the different electronegativity of the simple halide ions and their tetrahaloborate derivatives. The diazonium compound is quite stable in the presence of the highly electronegative tetrahaloborates and spontaneously decomposes at a certain excitation level, leading to phenyl cation intermediates. In the presence of simple halide ions, especially Br^-, I^-, and At^-, which exhibit smaller electronegativities than Cl^- and F^-, an electron-transfer reaction may proceed at quite lower excitation levels, thus leading to radical intermediates. Hey et al.[6] for example, have shown that diazonium tetrafluoroborates can be decomposed yielding radical intermediates in the presence of iodide. If the radical pair finds itself in a solvent cage, it may readily recombine to yield the halogenation product. It can be assumed that the lower the electronegativity of the halogen, the easier the electron transfer will be, and thus the smaller the interference with hydroxydediazoniation. In line with this explanation is the finding that an easy hydroxydediazoniation can be achieved in the presence of Cu catalysts.[17] The reaction is assumed to proceed via radical intermediates formed by electron transfer from copper-hexaaquo complexes and leads to fewer side products than the uncatalyzed reaction via phenyl cations.

According to these recent results a similar electron-transfer mechanism is proposed for iodo- and astatodediazoniation at low halide concentration levels.

$$PhN_2^+ + At^- \rightarrow (PhN_2^+At^-) \xrightarrow[\text{transfer}]{e^-} (Ph\cdot N_2At\cdot) \rightarrow PhAt + N_2$$

The heavier halides seem to have a tendency for complex formation with the diazonium group. At a sufficient thermal excitation level the electron transfer leads to the dissociation of nitrogen, while the phenyl and halogen radicals recombine.

This mechanism is similar to that proposed by Hodgson.[3] It is, however, concluded that the formation of trihalide ions is not necessary to yield halogenodediazonation. On the other hand, it is not questioned that additional processes may contribute to product formation at higher halide concentrations. The mechanism is in line with the observation of higher reaction yields with astatine than with iodine, since astatine has the smaller electronegativity. Furthermore, the intermediate formation of halide-diazonium complexes is also more favorable with astatine, as its polarizability is considerably greater. The few experiments which have been carried out to investigate the complex-forming ability indicate that it is quite similar to that of its lighter homologue iodine.[18,19] On the basis of atomic beam experiments it has been assumed that the polyvalency of astatine is more pronounced than that of iodine.[20] By comparison of the reactivity of AtCl and ICl with halobenzenes, we have recently shown[10,13] that the astatomonochloride tends to form complexes with the substrate more readily than ICl.

According to these results, the isomer distribution obtained in competition experiments with ortho, meta, and para isomers of diazonium salts may also be explained by complex formation. The stability of such complexes depends on the extent of covalency of the participating bonds. Thus an astatide-diazonium complex could be stabilized by additional polarization of the astatide ion. Such additional charge delocalization can be accomplished by substituents in ortho position to the diazonium group and should be dependent on their electronegativity. In contrast to the competition experiments (Table II), the results obtained with the individual substrates (Table I) cannot reflect differences in selectivity since the only competing anion OH^- is not expected to form stable complexes as is postulated for I^- and At^-. In the competition experiment the differences in isomer distribution can be attributed to different rate constants of complex formation for the individual competing substrates.

The somewhat lower ortho selectivity, observed with astatide relative to iodide, may be due to steric effects, which, in the case of a primary iodo substituent, allow ortho selectivity for attacking iodide, but lead to a statistical isomer distribution with astatide. In the case of toluene diazonium salts this tendency is continued, leading to para selectivity with astatide but a small ortho selectivity with iodide. However, different decomposition rates of the diazonium salt isomers may contribute to the observed isomer distribution. It has been shown that among chlorobenzenediazonium salts the ortho isomer is the most stable, while among the toluene derivatives the para isomer is the most stable one.[21] The different results obtained with astatine and iodine indicate, however, that the decomposition rates are not solely responsible for the observed distribution patterns.

References and Notes

(1) H. Zollinger, "Azo and Diazo Chemistry", Interscience, New York, 1961.
(2) H. Zollinger, *Acc. Chem. Res.*, **6**, 335 (1973).
(3) H. H. Hodgson, *Chem. Rev.*, **40**, 251 (1947).
(4) J. G. Carey, G. Jones, and I. T. Millar, *Chem. Ind.* (*London*), 1018 (1959).
(5) P. R. Singh and R. Kumar, *Aust. J. Chem.*, **25**, 2133 (1972).
(6) D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Commun.*, 1438 (1970).
(7) W. L. Hughes and J. Klinenberg, Report BNL 367 (S-27), 1955, p 42.
(8) G. Samson and A. H. W. Aten, Jr., *Radiochim. Acta*, **13**, 220 (1970).
(9) G.-J. Meyer, K. Rössler, and G. Stöcklin, *Radiochem. Radioanal. Lett.*, **21**, 247 (1975).
(10) G.-J. Meyer, Thesis, Universität zu Köln, 1978, Report Jül-1418, 1977.
(11) K. Rössler, W. Tornau, and G. Stöcklin, *J. Radioanal. Chem.*, **21**, 199 (1974).
(12) G.-J. Meyer and K. Rössler, *Radiochem. Radioanal. Lett.*, **25**, 377 (1976).
(13) G.-J. Meyer, K. Rössler, and G. Stöcklin, *Radiochem. Acta*, **24**, 81 (1978).
(14) G.-J. Meyer, K. Rössler, and G. Stöcklin, *J. Labelled Comp. Radiopharm.*, **22**, 449 (1976).
(15) A. M. Friedman, M. R. Zalutsky, W. Wung, F. Buckingham, P. V. Harper, G. H. Scherr, B. Wainer, R. L. Hunter, E. H. Appelman, R. M. Rothberg, F. W. Fitch, F. P. Stuart, and S. J. Simonian, *Int. J. Nucl. Med. Biol.*, **4**, 219 (1977).
(16) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961).
(17) T. Cohen, A. G. Dietz, Jr., and J. R. Miser, *J. Org. Chem.*, **42**, 2053 (1977).
(18) J. J. C. Schats and A. H. W. Aten, Jr., *J. Inorg. Nucl. Chem.*, **15**, 197 (1960).
(19) V. D. Nefedov, Yu. V. Norseev, Kh. Savlevich, E. N. Sinotova, M. A. Toropova, and V. A. Khalkin, *Dokl. Acad. Nauk SSSR*, **144**, 806 (1962).
(20) J. R. Grover, C. R. Iden, F. E. Schubert, and J. T. Muckermann, *Proc. Int. Conf. Phys. Electronic Atomic Collisions, 9th, 1975* (1975).
(21) M. L. Crossley, R. H. Kienle, and C. H. Benbook, *J. Am. Chem. Soc.*, **75**, 1400 (1940).

G.-J. Meyer, K. Rössler, G. Stöcklin*
Institut für Chemie 1 (*Nuklearchemie*)
der Kernforschungsanlage Jülich GmbH
Postfach 1913, D-5170 Jülich 1, West Germany

Received December 26, 1978

Flash Photolysis in the Adsorbed State: Pyrene on Porous Glass

Sir:

Although the absorption spectra[1-4] and photolysis[5-9] of molecules in the adsorbed state have been studied extensively by steady-state methods, no fast kinetic technique has been applied to such a system. In this communication, we report on the photochemistry of adsorbed pyrene using the flash photolytic technique. In particular, we describe the absorption

0002-7863/79/1501-3123$01.00/0

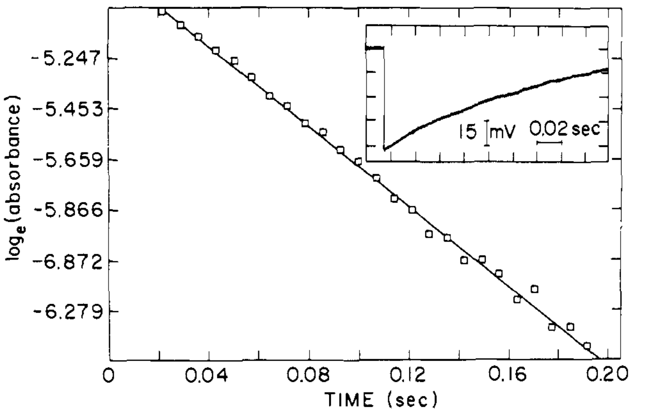


Figure 1. First-order plot of decay of transient absorbance (λ 520 nm). Insert depicts corresponding change of transmitted light level, I_0 = 1.0 V.

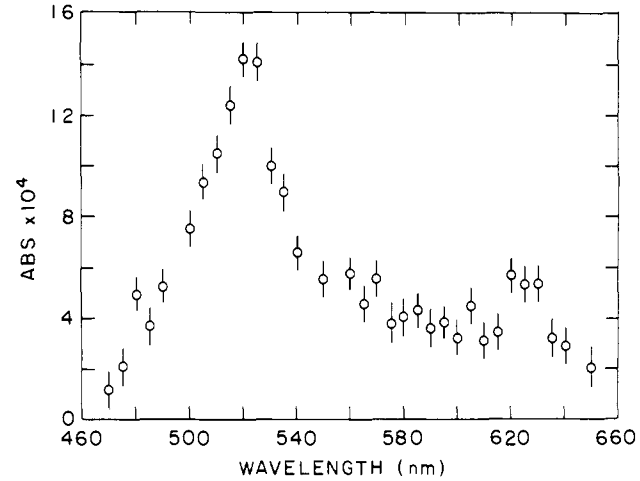


Figure 2. Transient absorption spectrum assigned to adsorbed triplet pyrene: band pass, 1 nm; pyrene surface coverage, 1.0 × 10^{-9} mol g^{-1}; pathlength, 4.0 cm. Error bars (±7 × 10^5 absorbance units) correspond to the mean error derived from repeated measurements of absorbance at 520 nm.

Table I. Triplet-Triplet Absorption Bands of Pyrene[a]

porous glass, <300 K	EPA,[b] 77 K	paraffin,[c] 300 K	n-hexane, 300 K	
			ref 19	ref 17
480 (0.35)	372 (0.1)	371.5 (0.3)	360 (0.06)	369
[500]		396.5 (0.5)	389 (0.3)	387
522 (1)	415 (1)	416 (1)	409 (1)	411
[590]	489 (0.15) 515 (s)	483 (0.2)	489 (0.06)	
625 (0.4)	525 (0.2)	519.5 (0.24)	520 (0.15)	520

[a] Units of wavelength are in nanometers; relative intensities are in parentheses; s indicates unresolved shoulder; square brackets refer to unresolved peaks. [b] Reference 18. [c] Reference 16.

spectrum and the kinetics of the decay of triplet pyrene adsorbed on porous glass.

Porous glass was chosen for this study because of its unique combination of the necessary properties of transparency, high surface area, and large total porosity, which is derived from a narrow distribution of large pores. The photolysis of pyrene has been studied by steady-state and flash techniques in both polar[10] and nonpolar[11] solvents and in aqueous micellar[12] systems. Leermakers et al. have investigated the photochemistry of adsorbed pyrene in a silica gel/cyclohexane slurry using steady-state techniques.[13] The spectra of the excited singlet-singlet absorption,[10] of the fluorescence and eximer emissions,[14] and of the cation[10,12] and anion[15] of pyrene are all known. The triplet-triplet absorption spectrum[16-19] and, in some instances, its rate of decay[18-22] have been measured. These known properties make pyrene a good choice to study photophysical and photochemical processes when a molecule is in the adsorbed state.

The porous glass sorbent (Corning Glass No. 7930) was a 4-cm length of 3-mm-diameter rod (surface area, 166 m^2 g^{-1}; total porosity, 0.25 cm^3 g^{-1}; and mean pore radius, 24.1 Å). Samples were cleaned initially with concentrated nitric acid and baked in an O_2 atmosphere at 500 °C for 8-12 h prior to adsorbing measured amounts of pyrene at ambient temperature from cyclohexane solutions. The samples were then outgassed at 130 °C to <3 × 10^{-6} Torr to remove the solvent. (Typical surface coverages employed were 1-9 × 10^{-9} mol m^{-2}.) Before use, the pyrene (KEK Laboratories) was purified by column chromatography. The samples were photolyzed at ambient temperatures using krypton lamps and a conventional flash photolysis system (Xenon Corp. Model 710).

A transient absorption, which was formed during the flash, was observed in the wavelength range 400-700 nm. This signal (Figure 1, insert) decayed according to first-order kinetics and the rate constant was independent of wavelength. The intensity of the absorbance, measured at 520 nm, increased linearly with flash intensity (electrical energy input, 20-160 J), while the rate of decay remained unchanged. On addition of oxygen, a known triplet quencher, the signal was no longer observed, but, when the adsorbed oxygen was removed by suitable degassing under vacuum, the signal reappeared at its original intensity (within experimental error). From these observations, the transient absorption was assigned to that of triplet pyrene formed during the excitation flash.

At ambient temperature, the first-order rate constant for triplet decay was 7.95 ± 0.07 s^{-1}, corresponding to an average lifetime of 126 ± 2 ms (Figure 1). Comparable lifetimes observed for pyrene in other systems are 1.8 ms in *n*-hexane at 300 K,[19] 333 ms in viscous paraffin at 300 K,[20] 500-700 ms in EPA at 77 K,[18,21] and 400 ms in plastic at 300 K (phosphorescence measurement).[21] It is evident that the triplet lifetime is much longer at ambient temperature in the adsorbed state compared with that in hydrocarbon solutions. Preliminary studies showed that the triplet lifetime was affected by temperature as well as by surface environment, which varied according to the outgassing history of the particular sorbent sample.

The transient absorption spectrum, which was measured 0.5 ms after initiation of the excitation flash to avoid complications due to a short-lived emission from the sorbent, is shown in Figure 2. No signal was detected at wavelengths in the range of 380-460 nm, where the strongest triplet-triplet absorption bands occur for pyrene in solution. The wavelengths of the resolved bands observed for adsorbed triplet pyrene are listed in Table I, together with those which have been reported for hydrocarbon solution and for EPA glass at 77 K. The surface concentration of the pyrene was kept low (1.0 × 10^{-9} mol g^{-1} or 1.5 × 10^5 Å^2/molecule) to ensure maximum spectral resolution. At greater surface coverages, spectral resolution decreased owing to band broadening, usually more evident in the spectra of molecules in the adsorbed state. However, the dominant absorption peaks at 520 and 625 nm were still readily apparent.

A striking observation is the large red shift (~100 nm, ~0.8 eV) of the triplet absorption in the adsorbed state compared with that in solution. This large shift to lower energy suggests a strong interaction of the more polar triplet states of pyrene with the sorbent surface. On the other hand, the singlet absorption bands ($S_n \leftarrow S_0$), although slightly red shifted with respect to the corresponding bands in the gas phase (~8 nm), are close to those measured in hydrocarbon solvents ($\lesssim$2 nm). The measurement of the weak phosphorescence emission from adsorbed pyrene, currently being carried out, will help to clarify these shifts in the triplet energy states.

The results demonstrate that the flash photolytic technique can be extended to photolysis in the adsorbed state and that significant changes can be anticipated in the lifetime, spectra, and, perhaps, the chemistry of adsorbed excited species. Work is in progress to extend this investigation to shorter times using a laser flash and to study the behavior of radical and ionic transients in the adsorbed state.

Acknowledgment. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. EY76-C-02-0016.

References and Notes

(1) C. H. Nicholls and P. A. Leermakers, *Adv. Photochem.*, **8**, 315–336 (1971).
(2) A. Terenin, *Adv. Catal.*, **15**, 227–284 (1964).
(3) H. P. Leftin and M. C. Hobson, Jr., *Adv. Catal.*, **14**, 115–201 (1963).
(4) M. Robin and K. N. Trueblood, *J. Am. Chem. Soc.*, **79**, 5138 (1957).
(5) P. K. Wong, *Photochem. Photobiol.*, **19**, 391 (1974).
(6) A. J. Tench and G. T. Pott, *Chem. Phys. Lett.*, **26**, 590 (1974).
(7) C. Yun, M. Anpo, and Y. Kubokawa, *J. Chem. Soc., Chem. Commun.*, 665 (1977).
(8) M. Anpo, T. Wada, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **50**, 31 (1977), and references therein.
(9) K. Otsuka, M. Fukaya, and A. Morikawa, *Bull. Chem. Soc. Jpn.*, **51**, 367 (1978).
(10) J. T. Richards, G. West, and J. K. Thomas, *J. Phys. Chem.*, **74**, 4137 (1970).
(11) G. Beck and J. K. Thomas, *J. Chem. Phys.*, **57**, 3643 (1972).
(12) S. C. Wallace, M. Grätzel, and J. K. Thomas, *Chem. Phys. Lett.*, **23**, 359 (1973).
(13) L. D. Weis, T. R. Evans, and P. A. Leermakers, *J. Am. Chem. Soc.*, **90**, 6109 (1968).
(14) J. T. Birks, "Photophysics of Aromatic Molecules", Wiley-Interscience, New York, 1970.
(15) S. C. Wallace and J. K. Thomas, *Radiat. Res.*, **54**, 49 (1973).
(16) G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A*, **245** 283 (1958).
(17) G. Porter and M. W. Windsor, *Disc. Faraday Soc.*, **17**, 178 (1954).
(18) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, 1589 (1954).
(19) W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, **4**, 20 (1969).
(20) B. Stevens and M. S. Walker, *Proc. R. Soc. London, Ser. A*, **281**, 420 (1964).
(21) R. E. Kellogg and R. P. Schwenker, *J. Chem. Phys.*, **41**, 2860 (1964).
(22) T. Medinger and F. Wilkinson, *Trans. Faraday Soc.*, **62**, 1785 (1962).

Paul L. Piciulo, James W. Sutherland*
Department of Energy and Environment
Brookhaven National Laboratory, Upton, New York 11973

Received January 22, 1979

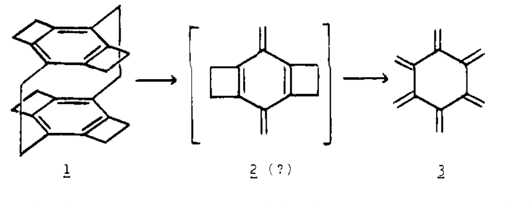
[2.2.2.2.2](1,2,3,4,5)Cyclophane

Sir:

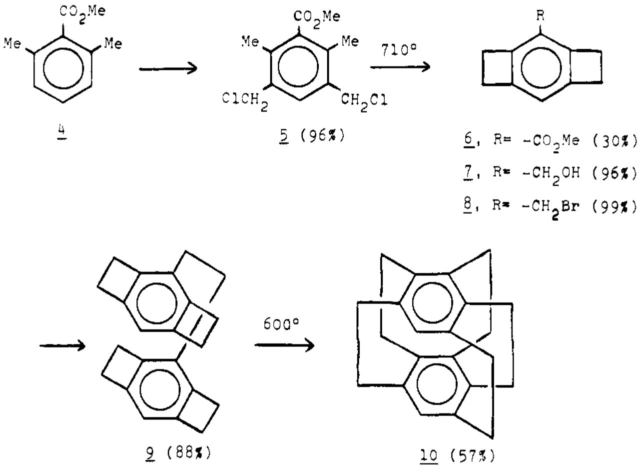
Di-*p*-xylylene and its crystal structure were first reported just 30 years ago.[1] The importance of this observation was immediately recognized by Cram,[2] who introduced the cyclophane nomenclature and systematically prepared a large number of structures having aromatic rings held face to face in rigid cages. The value of cyclophanes as models for testing all manner of questions of bonding, strain, and π–π electron interactions has resulted in a phenomenal growth of interest in the field.[3-5] From the beginning, one of the most intriguing questions has been the nature of the π-electron interaction when two aromatic rings are crowded together face to face and the limit to which such crowding can be forced. Whereas the mean planar distance between benzene rings in [2.2]paracyclophane is 3.09 Å,[6] it is only 2.80 Å in [2.2.2](1,3,5)cyclophane-1,9-diene,[7] and 2.69 Å in [2.2.2.2](1,2,4,5)cyclophane.[8] The theoretical calculations of Lindner predict that [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane will have a mean planar distance between rings of only 2.60 Å with the molecule having a total strain energy of 60–79 kcal/mol.[9] Thus, the change in geometry and strain energy as additional bridges are added is of special interest.

The preparation of multibridged cyclophanes in the normal way of adding a bridge at a time is exceedingly long, and so the synthesis of higher examples of multibridged cyclophanes has awaited the development of new methods. We now report that the dimerization of benzocyclobutenes provides an efficient and relatively short method for synthesizing multibridged cyclophanes. In this communication we describe the preparation of [2.2.2.2.2](1,2,3,4,5)cyclophane (**10**) and, in the accompanying communication, the synthesis of [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane (superphane).[10]

The concept of using the dimerization of benzocyclobutenes to introduce multiple bridges in cyclophanes was first proposed for the case of [2.2](3,6)benzo[1,2;4,5]dicyclobutenophane (**1**).[11] Unfortunately, pyrolysis of **1** led to hexaradialene (**3**),[12] presumably due to the preferential cleavage to the *p*-xylylene intermediate **2** rather than to the desired multi-*o*-xylylene intermediate. Subsequently, the basic idea of benzocyclobutene dimerization to prepare multibridged cyclophanes was demonstrated by a simple, practical synthesis of [2.2.2.2](1,2,4,5)cyclophane.[13] Therefore, we turned our attention to the benzycyclobutene derivative **9**, which can no longer undergo thermal cleavage to a *p*-xylylene intermediate.



As summarized in the reaction scheme, chloromethylation of methyl 2,6-dimethylbenzoate (**4**)[14] readily gave **5** as white crystals, mp 105–106 °C.[15] Gas-phase pyrolysis of **5** at 710 °C and 10^{-2} Torr, following the procedure described previously,[11] led to **6** (white crystals, mp 98.5–99.5 °C). Reduction of **6** with lithium aluminum hydride yielded **7** (white crystals, mp 109–110 °C), which on treatment with phosphorus tribromide gave **8** (white crystals, mp 60–62 °C). Conversion of **8** to the Grignard by treatment with magnesium in tetrahydrofuran followed by addition of anhydrous ferric chloride gave the coupling product **9** as white crystals: mp 198.5–199.5 °C: NMR δ 6.63 (2 H, s, Ar H), 3.04 (16 H, s, -CH_2), and 2.77 (4 H, s, -CH_2). Pyrolysis of 174 mg of **9** at 600 °C and 0.05 Torr yielded a white solid which, after chromatography over silica gel using a benzene-hexane mixture for elution, gave 100 mg (57%) of [2.2.2.2.2](1,2,3,4,5)cyclophane (**10**) as white crystals: mp 334–336 °C dec; NMR δ 6.05 (2 H, s, Ar H), 2.92 (4 H, s, -CH_2), 2.82 (8 H, d, J = 2.5 Hz), and 2.56–3.33 (8 H, AA′BB′, -CH_2); UV (THF) λ_{max} 294 (ϵ 352) and 313 nm



0002-7863/79/1501-3125$01.00/0