Figure 1. B shows regions of the normal ^{1}H FT spectrum (270 MHz) of 1 (0.1 M in benzene-d_6); A shows the corresponding skew projections of the 2-D J spectrum (plotted in the power mode with sine bell and exponential multiplication of the time-domain signals in the t_2 and t_1 dimensions, respectively) in which each proton appears to be completely proton decoupled and only the chemical shifts and ^{1}H-^{19}F couplings are observed. Each partial J spectrum shown in C is only a function of the appropriate ^{1}H-^{1}H coupling constants; since instrumental line broadening in the t_1 dimension is now minimized, the ^{1}H-^{1}H coupling constants can be accurately measured.
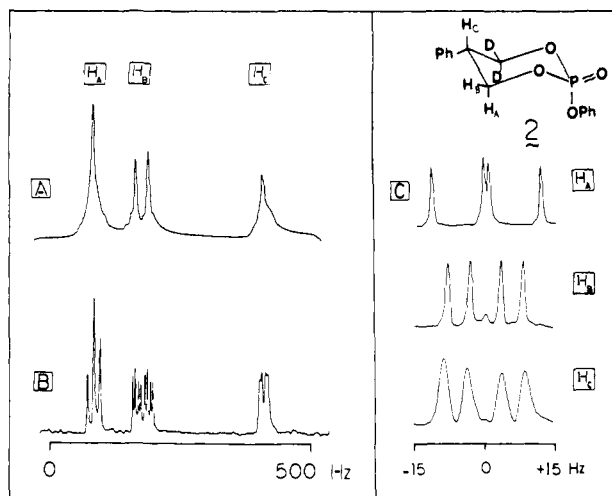

Figure 2. The high-field region of the conventional ^{1}H FT spectrum (270 MHz) of 2 (0.1 M in benzene-d_6) is shown in B. The corresponding skew projection, A, shows the ^{1}H$_B$-^{31}P coupling, while all ^{1}H-^{1}H couplings are suppressed; note that the lines show broad "tails" owing to use of the absolute-mode display. The partial J spectra of the protons shown in C give the ^{1}H-^{1}H couplings.

heteronuclear couplings still remaining.

The spectra of the difluoro sugar 1 shown in Figure 1 serve to illustrate the distinction between ^{1}H-^{19}F and ^{1}H-^{1}H couplings. Regions of the conventional ^{1}H FT spectrum are shown in Figure 1B; although the large geminal ^{1}H-^{19}F couplings ($\sim$50 Hz) are obvious, distinction between the other couplings is less clear. In the skew projections of the corresponding regions shown in Figure 1A, all of the homonculear (^{1}H-^{1}H) couplings have been suppressed, leaving only the ^{1}H-^{19}F splittings, which can easily be measured. Although the magnitudes of the ^{1}H-^{1}H couplings could now have been interpolated from the normal spectrum, more convenient and accurate measurements were obtained from the partial J spectra (Figure 1C). Owing to the refocussing of the magnetic field inhomogeneity effects at the end of the evolution period, the line widths in the partial J spectra are mainly determined by spin-spin

relaxation times rather than instrumental effects;[11] as a typical example of the resultant resolution enhancement, the small difference between the two vicinal couplings for H-3 ($J_{3,2} = 9.02$, $J_{3,4} = 9.45$ Hz) is clearly resolved in Figure 1C.

Figure 2 illustrates similar studies of 2, which exhibits ^{1}H-^{1}H and ^{1}H-^{31}P couplings. Although the coupling of phosphorus to the equatorial proton ($J = 22.8$ Hz) can be measured from the skew projection (Figure 2A), coupling to the axial proton (1.4 Hz) is not resolved; this loss of resolution is mainly due to both the instrumental line broadening and poor digital resolution in the f_2 dimension.[3,12]

It is clear that the methods summarized here have the merit that scalar couplings from any number of different heteronuclei may be simultaneously suppressed, regardless of their chemical shift separation, without the need for any modification of the spectrometer or probe; thus for example, simultaneous decoupling of both ^{19}F and ^{31}P could be effectively achieved. We believe that this will lead to a number of important chemical applications.

References and Notes

(1) W. P. Aue, E. Bartholdi, and R. R. Ernst, *J. Chem. Phys.*, **64**, 2229 (1976).
(2) W. P. Aue, J. Karhan, and R. R. Ernst, *J. Chem. Phys.*, **64**, 4226 (1976).
(3) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. L. Turner, *J. Magn. Reson.*, **26**, 133 (1977).
(4) Digital summation of selected traces of a 2-D J spectrum.
(5) R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, **54**, 301 (1971).
(6) K. Nagayama, P. Bachmann, K. Wüthrich, and R. R. Ernst, *J. Magn. Reson.*, **31**, 133 (1978).
(7) G. Bodenhausen, R. Freeman, G. A. Morris, and D. L. Turner, *J. Magn. Reson.*, **31**, 75 (1978).
(8) R. Freeman and H. D. W. Hill, "Dynamic nuclear Magnetic Resonance", F. A. Cotton and L. M. Jackman, Eds., Academic Press, New York/London, 1975, Chapter 5.
(9) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).
(10) A projection onto an axis such that $\partial f_2/\partial f_1 = -1$; if f_1 and f_2 axes were plotted on the same scale this axis would be set at 45° to the f_2 axis.
(11) G. Bodenhausen, R. Freeman, R. Niedermeyer, and D. L. Turner, *J. Magn. Reson.*, **24**, 291 (1976).
(12) To make efficient use of the computer storage and operating capacity it is usually advantageous to limit the digital resolution in the f_2 dimension.

Laurance D. Hall,* Subramaniam Sukumar

Department of Chemistry, University of British Columbia Vancouver, British Columbia, Canada, V6T 1W5

Reaction of Aromatic Diazonium Salts with Carrier-Free Radioiodine and Astatine. Evidence for Complex Formation

Sir:

The understanding of the dediazoniation process is complicated by the fact that its mechanism is not unique but quite dependent on the reaction conditions.[1,2] Dediazoniation can occur by both ionic and free-radical paths. In particular, in the case of iododediazoniation, which may be carried out in acidic aqueous solutions without major hydrolysis even in the absence of a catalyst, several mechanisms have been discussed.[3-6] All of them, however, draw an analogy to the Sandmeyer type by assuming a redox step with radical intermediates.

Tracer experiments with radiohalogens in the picomole region can provide new information on the question of complex formation, which should be particularly favorable in the case of the heaviest halogen astatine. Since this is a radioelement with rather short-lived isotopes (^{211}At, $T_{1/2} = 7.2$ h), only

Table I. Radiochemical Yields (Percent) of Astato- and Iododediazoniation of Benzene Derivatives (0.3 M Solutions Heated for 5 Min at 80 °C)

substrate	^{211}At	^{131}I
o-, *m*-, *p*-fluoroaniline	Σ 40 ± 20	Σ 6.4 ± 2.5
o-chloroaniline	16 ± 4	7
m-chloroaniline	12 ± 2	7
p-chloroaniline	10 ± 3	6
o-, *m*-, *p*-chloroaniline	Σ 16 ± 4	Σ 5.1 ± 0.9
m-bromoaniline	26 ± 10	8
o-, *m*-, *p*-bromoaniline	Σ 19 ± 4	Σ 17.0 ± 1.5
o-, *m*-, *p*-iodoaniline	Σ 14 ± 4	3.9 ± 1.9
o-methylaniline	12	6
m-methylaniline	16	6
p-methylaniline	17	8
o-, *m*-, *p*-methylaniline	Σ 20 ± 7	Σ 6.3 ± 2.2
aniline	18.7 ± 4.5	6 ± 3
	12 ± 3[a]	5 ± 3[a]

[a] Competition experiment with a mixture of ^{211}At$^-$ and practically carrier-free ^{131}I$^-$.

10^{-13}–10^{-12} mol are available in a typical experiment.

Dediazoniation followed by incorporation of astatine was reported by Hughes et al.[7] and Samson and Aten.[8] Systematic studies of the astatodediazoniation reaction and a comparison with iododediazoniation under comparable conditions have been carried out in this laboratory.[9,10] Despite the extremely low halide concentration the reaction is quite selective in aqueous solutions and occurs with reasonable yields.

^{211}At was produced at the isocronous cyclotron of the KfK Karlsruhe as described previously.[11,12] A 0.1-mmol quantity of aromatic amine (*o*-, *m*-, and *p*-XC$_6$H$_4$NH$_2$ (X = H, F, Cl, Br, I, CH$_3$)) purified by vacuum distillation was diazonized in 0.2 mL of 6 N HCl at −5 °C by addition of 40 μL of 2.5 M NaNO$_2$ solution. Any excess of NaNO$_2$ was destroyed by 3 mg of urea. After the addition of ^{211}At$^-$ (300 μCi in 50 μL of 0.1 M Na$_2$SO$_3$ solution), the reaction mixture was heated in ∼5–6 min to 80 °C. The solution was cooled and extracted twice with 1 mL of ether. The ether layers were washed with 2 M NaOH solutions, dried over CaCl$_2$, and analyzed by gas chromatography. The astatohalobenzenes were analyzed on 1-m glass columns packed with Chromosorb W-AW-DMCS, loaded with 6% Bentone 38 and 20% silicon oil DC 200, at 120 °C, and the astatotoluenes were analyzed on 4-m glass columns packed with 5% azoxidianisol on Chromosorb W-AW-DMCS, at 100 °C. The carrier gas was He at a flow rate of 100 mL/ min. For the retentions of *o*-, *m*-, and *p*-chloro-, -bromo-, and -iodoastatobenzenes, cf. ref 9; for those of *o*-, *m*-, and *p*-fluoroastatobenzenes and astatotoluenes, cf. ref. 13. Dediazoniation experiments were carried out either with the individual ortho, meta, and para isomers or with equimolar amounts of ortho, meta, and para isomer mixtures under competitive conditions. For a comparison, experiments were carried out with 30 μL of ^{131}I$^-$ solutions (10 mCi mL^{-1} = 10^{-7} mol of NaI mL^{-1}). Furthermore, competition experiments with simultaneous addition of ^{211}At$^-$ and ^{131}I$^-$ were also conducted.

The thermal decomposition of the diazonium salts led to an 80% fraction of labeled organic products, which could be ex-

tracted with ether. Half of this activity could, however, be washed out with aqueous NaOH and may be attributed to products formed in a side reaction between inorganic At species and phenol derivatives. About 40% of the remaining organic activity (16% of total) consisted of the astatohalobenzenes. The greater fraction (24% of total) was not eluted from the gas chromatographic column, thus indicating an oligomer or polymer fraction. Reinjection of the separated products gave recovered yields of >90%, indicating that the astatohalobenzenes and astatotoluenes were stable under the separation conditions. The overall yields of astato- and iododediazoniation reactions at carrier-free concentration levels are given in Table I.

The yield for all astatohalobenzenes and -toluenes was rather constant and unaffected by the nature of the diazonium compound, its isomeric form, and the number of isomers used at a time. Only astatofluorobenzenes were obtained at higher yields, however, with quite a large variation over several experiments. Generally the yields were significantly higher with ^{211}At$^-$ than with ^{131}I$^-$.

The isomer distribution of *o*-, *m*-, and *p*-astatohalobenzenes and -toluenes obtained in competition experiments is listed in Table II. Although the experiments with single compounds gave quite similar yields with each isomer, the competition experiments exhibited a very selective isomer distribution. At$^-$ reacts preferentially with ortho isomers of fluoro-, chloro-, and bromoanilines. The iodo compounds were, however, statistically substituted and in the case of diazonized toluidines a para selectivity was observed. This allows the conclusion that the ortho substitution is dependent on the electronegativity of the substituent. A similar trend was also found with ^{131}I$^-$. All diazonized aniline derivatives investigated exhibited an ortho selectivity which again became smaller with decreasing electronegativity of the substituent.

Considering the extremely low concentration of At$^-$ and I$^-$ in the above experiments ($\leq$10^{-12} and 10^{-8} mol/L, respectively), it is surprising to find 10–20% astato- and 6–10% iododediazoniation, since hydrolysis of the diazonium compound is a competing process under these reaction conditions. Even higher yields have been obtained in the synthesis of 5-astatouracil (up to 35%)[14] and in the synthesis of *p*-astatobenzoic acid.[15] The currently proposed mechanisms for iododediazoniation, however, do not adequately explain the present results since the formation of trihalide ions[3,4] is impossible at these halide concentrations, as is any mechanism that includes chain-type reaction steps.[5]

In the series of halogenodediazoniations from fluorine to iodine, the reaction becomes constantly smoother with less interference of hydroxydediazoniation. Our competition experiment utilizing a mixture of astatide and iodide supports and extends this sequential character of halogenodediazoniations. Therefore it seems reasonable to interpret this type of reaction by considering the sequentially changing properties of the halogens. The factors which might cause the different reactivity of the halogen ions in the series from fluoride to astatide are the decreasing electronegativity and strength of hydrate shell as well as the increasing polarizability and nucleophilicity. Olah and Tolgyesi[16] mentioned that the intermediacy of phenyl cations may be a special feature of the

Table II. Relative Isomer Distribution (Percent) of Astato- and Iodobenzene Derivatives from Dediazoniation of an Equimolar Mixture of Ortho-, Meta-, and Para-Diazonium Salts (0.3 M Solutions Heated for 5 Min at 80 °C)

substrates	astatohalobenzenes			iodohalobenzenes		
	ortho	meta	para	ortho	meta	para
o-, *m*-, *p*-fluoroaniline	65 ± 3	25 ± 3	10 ± 3	82 ± 3	11 ± 3	7 ± 4
o-, *m*-, *p*-chloroaniline	50 ± 3	22 ± 3	28 ± 3	79 ± 2	3 ± 1	18 ± 1
o-, *m*-, *p*-bromoaniline	44 ± 3	26 ± 3	30 ± 3	59 ± 3	24 ± 1	17 ± 1
o-, *m*-, *p*-iodoaniline	34 ± 4	34 ± 4	32 ± 4	64 ± 6	27 ± 6	9 ± 1
o-, *m*-, *p*-methylaniline	13 ± 7	22 ± 5	64 ± 10	50 ± 6	35 ± 5	15 ± 4

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.

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

$$\rightarrow PhAt + N_2$$
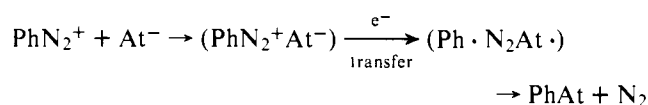
The heavier halides seem to have a tendency for complex formation with the diazonium group. At a sufficient thermal excitation level the electron transfer leads to the dissociation of nitrogen, while the phenyl and halogen radicals recombine.

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

II) 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 iodine. 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

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