Communications to the Editor

On the Rate of Site–Site Interactions in Functionalized Polystyrenes

Sir:

Reagents attached to insoluble, cross-linked polystyrene supports must experience reduced mobility with respect to their counterparts in bulk solution. Evidence for[1] and against[2] this site–site insulation or pseudodilution leaves questions regarding the rates at which intrapolymeric encounters occur. Here we report experiments which bear on this issue.

Our technique involves generating a self-destructive species on a given support and determining its rate of disappearance. Specifically, we examined the polymer-bound acylating agent—nucleophile system **2c.** Glycyl transfers within the resin produce peptides of glycine **3,** bound as their C-terminal nitrophenyl esters; cyclization then releases peptides **4** into solution.[3] See Scheme I.

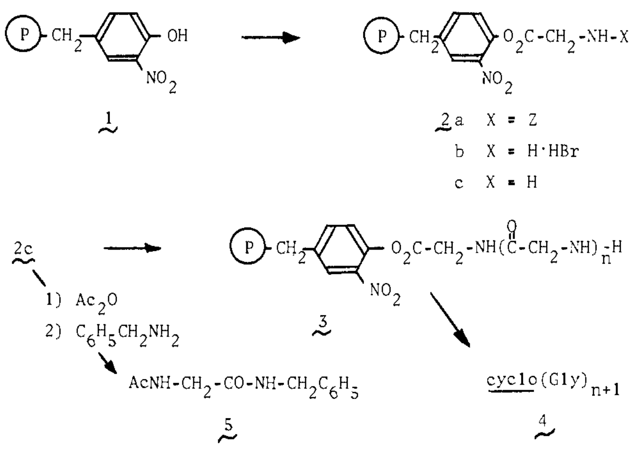
Polymer-bound nitrophenol **1,** 1 mequiv/g was prepared by Patchornik's procedure[4] from 4% cross-linked polystyrene (Rohm & Haas XE-305). Radioactive glycine was attached as its benzyloxycarbonyl (Z) derivative **2a,** 0.8 mequiv/g, using carbodiimide. N deblocking with HBr–HOAc gave the stable salt **2b.**

Suspensions of **2b** in DMF were treated with excess Et_3N or *N*-methylmorpholine to ensure that the generation of **2c** was rapid and complete.[5] Radioactivity was quickly released into solution during the first 30 min (50%) and then more slowly[6] (~65% after 2 days). Isotope dilution established that 20% of the activity released was diketopiperazine (**4,** $n = 1$) and <2% was glycine (little, if any, hydrolysis occurs). The remaining activity in solution was presumably in the form of cyclic oligomers of glycine (**4,** $n > 1$) since the ninhydrin test proved negative.

The extent of disappearance of monomer **2c** could be determined by quenching the intrapolymeric acyl transfers with Ac_2O. Subsequent treatment with benzylamine releases any remaining **2c** in the form of the *N*-benzylamide of aceturic acid **5.** Isotope dilution for **5** revealed that, 30 min after Et_3N was added, <5% of the original activity on the solid phase was the monomer **2c,** whereas, after 5 min, 20% was the monomer. When **2b** was treated simultaneously with Et_3N and Ac_2O, followed by benzylamine, 80% monomer **2c** was trapped.[7] This demonstrates that glycyl transfers within the polymer occur even in the presence of excess acylating agents in solution.

Initially, the disappearance of monomer **2c** should resemble a second-order process. Interaction of two sites gives **3** ($n = 1$) which can cyclize and release diketopiperazine into solution. However, **3** ($n = 1$) may also engage in further reactions with monomer sites, acting either as a nucleophile or as an acylating agent. Evidence that these secondary processes occur may be inferred from the low yield of diketopiperazine. The ensemble of polymer-bound acylating agents and nucleophiles thus generated and the large numbers of their possible intrapolymeric reactions preclude kinetic analysis. The empirical value of 1–2 min for the half-life of **2c,** assuming a second-order process for its disappearance, can be derived from the quenching experiments. If acyl transfers between sites of **2c** do not occur at every encounter, this half-life corresponds to a lower limit for the encounter frequencies of reagents attached to such polymers. Remarkably, this figure agrees well with that derived independently by Mazur[8] for the dimerization rate of polymer-bound benzyne.

Scheme I



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(3) M. Fridkin, A. Patchornik, and E. Katchalski, *J. Am. Chem. Soc.*, **87,** 4646 (1965). Azlactone formation may also release the polyglycines from the resin, but this also requires at least one intrapolymeric acyl transfer of **2c**.

(4) L. Kalir, M. Fridkin, and A. Patchornik, *Eur. J. Biochem.*, **42,** 151 (1974).

(5) Control experiments with **2a** established that these bases did not act as nucleophilic catalysts under these conditions; cf. J. Rebek, D. Brown, and S. Zimmerman, *J. Am. Chem. Soc.*, **97,** 454 (1975).

(6) Unlike **2a** which reacted readily and completely (>95%) with benzylamine in solution, samples of **2b** which had been exposed to Et_3N for this time failed to release additional radioactive material, even under forcing conditions.

(7) Experiments using lower levels of polymer loading (0.01 mequiv/g) gave similar results. The "mobility" of groups on such supports has been shown to decrease with increased cross-linking (S. L. Regen, *J. Am. Chem. Soc.*, **96,** 5275 (1974)), and with charge type (G. Crosby and M. Kato, *ibid.*, **99,** 278 (1977)).

(8) S. Mazur and P. Jayalekshmy, *J. Am. Chem. Soc.*, elsewhere in this issue.

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Synthesis and Characterization of (Pentafluorosulfur)acetylenes

Sir:

The synthesis and properties of compounds containing pentafluorosulfur groups have been a matter of concern for some time,[1] and renewed interest in such materials is evident from recent publications.[2] As an extension of earlier work in

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this laboratory dealing with reactions between pentafluorosulfur halides and olefins,[3] we have investigated reactions of SF_5Br with selected acetylenes in an attempt to synthesize new SF_5-substituted acetylenic monomers. In this paper, we describe the synthesis and characterization of the novel compounds, bis(pentafluorosulfur)acetylene, $SF_5C{\equiv}CSF_5$, and (pentafluorosulfur)trifluoromethylacetylene, $SF_5C{\equiv}CCF_3$.

Millimole quantities of SF_5Br and $SF_5C{\equiv}CH$, the only previously known (pentafluorosulfur)acetylene,[4] reacted readily in sealed Pyrex vessels at 105 °C for 3 h to give a 75% yield of the 1:1 addition product $SF_5CBr{=}CHSF_5$ (I). This compound, which is the first example of a bis(pentafluorosulfur)ethylene, is a clear liquid with a vapor pressure of $\sim$11 Torr at 25 °C. It was isolated by vacuum distillation through a trap at -23 °C into a collection trap at -45 °C. The infrared spectrum contained the characteristic absorptions of olefinic C—H and C=C stretching vibrations at 3115 and 1610 cm^{-1} and the very intense absorptions of S–F vibrations at 895, 890, and 605 cm^{-1}. The mass spectrum, recorded on a CVC TOF instrument, showed two weak, but distinct, peaks at 360 and 358 mu corresponding to the parent ions with the bromine isotopes. Additional principal peaks were found at 233 and 231 ($SF_5C_2HBr^+$), 127 (SF_5^+), 106 and 104 (C_2HBr^+), and 89 (SF_3^+). In the ^{19}F NMR spectrum, two pairs of complex doublets and an 18-line pattern appeared downfield from the internal Freon-11 resonance. The doublets (δ -64.7 and -60.4 ppm; $J \approx 155$ and 154 Hz)[5] were assigned to the four equatorial fluorine atoms whose resonances were split by coupling with the axial fluorine atom in each SF_5 group. The 18-line pattern, whose most intense peak had a chemical shift of -73.2 ppm, was an overlap of two 9-line resonances arising from AB_4 coupling of the axial fluorines with those in the equatorial positions. These data were consistent with the expected presence of two nonequivalent SF_5 groups in the molecule and further suggested that only one isomer was formed. Additional support for this conclusion was obtained from ^1H NMR data which contained a regular pentet (τ 2.30, $J = 6.8$ Hz) originating from coupling with a geminal SF_5 group. The lack of coupling between the hydrogen atom and the second SF_5 group suggested a cis relationship between H- and SF_5-, leading to the conclusion that the SF_5 groups are trans to each other.

Dehydrobromination of I by KOH occurred readily at ambient conditions to give a 64% yield of the novel bis(pentafluorosulfur)acetylene, $SF_5C{\equiv}CSF_5$ (II), which is of particular interest as the SF_5 analogue of hexafluorobutyne. The identity of the material was confirmed by gas-phase molecular weight measurements (found, 278.5; theory, 278.1) and spectroscopic data. In the gas-phase infrared spectrum, a weak absorption at 2220 cm^{-1} was assigned to the C≡C stretching vibration, and the very strong bands at 930, 920, and 605 cm^{-1} to S–F vibrations. The ^{19}F NMR spectrum in Freon-11 contained only one AB_4 pattern (δ_A -67.1 and δ_B -79.7 ppm ($J \approx 148$ Hz))[5] which was consistent with equivalent SF_5 groups. A relatively simple mass spectral fragmentation pattern contained a very weak parent ion at 278 mu, together with major fragments at 259 ($S_2F_9C_2^+$), 151 ($SF_5C_2^+$), 127 (SF_5^+), and 89 (SF_3^+). The experimentally determined vapor-pressure equation, $\log P(\mathrm{mm}) = 7.76 - (1582/T)$, yielded an extrapolated boiling point of 51.0 °C, $\Delta H_{\mathrm{vap}} = 7.24$ kcal/mol, and $\Delta S_{\mathrm{vap}} = 22.3$ cal/K.

The mixed (pentafluorosulfur)trifluoromethylacetylene, $SF_5C{\equiv}CCF_3$ (III), was synthesized by a route similar to that of II. We found, as did Gard and co-workers,[6] that SF_5Br reacted with 1,1,1-trifluoropropyne to give the monoaddition product $SF_5CH{=}CBrCF_3$ (IV). This, in turn, underwent dehydrobromination readily with KOH at ambient conditions to give the desired $SF_5C{\equiv}CCF_3$ (III). A molecular weight of 220.9 (theory, 220.1) was determined by gas density measurements and was in good agreement with a weak parent ion observed at 220 mu in the mass spectrum. The remainder of the spectrum contained a simple fragmentation pattern with major peaks at 201 ($SC_3F_7^+$), 127 (SF_5^+), 112 ($C_3F_4^+$), 108 (SF_4^+), 93 ($C_3F_3^+$), 89 (SF_3^+), and 69 (CF_3^+). The gas-phase infrared spectrum contained a weaker C≡C stretching vibration at 2295 cm^{-1} than that observed in the bis(SF_5) compound II, along with very intense bands at 1270, 1200, 945, 920, 850, and 625 cm^{-1} resulting from C–F and S–F vibrations. ^{19}F NMR data were also consistent with the presence of an SF_5 and a CF_3 group within the molecule as evidenced by the AB_4 pattern (δ_A -68.0 and δ_B -78.8 ppm ($J \approx 149$ Hz) relative to internal Freon-11),[5] and a regular pentet at δ $+53.7$ ppm arising from coupling of the CF_3 resonance with the SF_4 portion of the SF_5 group. At ambient conditions, the compound is a gas with a boiling point of 14.4 °C, and an enthalpy and entropy of vaporization of 5.12 kcal/mol and 17.8 cal/K as calculated from the vapor pressure equation, $\log P(\mathrm{mm}) = 6.77 - (1118/T)$. It is interesting that the boiling point of this compound is about halfway between that of 51.0 °C for the bis(SF_5) compound II and -24.6 °C for the bis(CF_3) molecule, hexafluorobutyne. From this, it can be seen that the replacement of a CF_3 with an SF_5 group in this series of acetylenes is responsible for an increase of 35–40 °C in the boiling point of the compound.

We are continuing our investigations of these unique compounds to gain some insight into their chemistry and into the nature of polymeric materials that may be derived from them.

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(5) Chemical shift values are given for the most intense line of the A and B portions of the AB_4 spectra and J_{AB} values are estimated from the basic doublet pattern of the B portion.

(6) G. L. Gard, private communication.

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A Dynamical Equilibrium between Ion Pairs of Aromatic [9]Annulene Anion and of Olefinic Nonafulvene Structure, Respectively

Sir:

The ion-pair character of organometallic compounds R^-M^+ [1] and of enolates $R_2C{=}CRO^-M^+$ [2] has been extensively studied in recent years. Since the structure (and the reactivity) of these species is a function of the solvent S, the temperature, the concentration, the gegenion M^+, and the nature of groups R, one is usually faced with a rather complex situation. Furthermore, differentiation of the various ion pairs can be difficult because of their structural similarity.

We report the case of a compound which exists in tetrahydrofuran (THF) in the form of two ion pairs which are entirely different structurally and easily detectable by means of ^1H NMR spectroscopy: the sodium enolate (**1**) with its olefinic nonafulvene structure and the $CH_3C(O)$-substituted sodium cyclononatetraenide (**2**) which is aromatic. The dynamic equilibrium **1** $\rightleftharpoons$ **2** is shifted from **1** to **2** on lowering the tem-