

silver bromide was filtered and washed with acetonitrile; the filtrate was poured into 450 mL of water. The ether extract was washed with water and dried ( $\text{Na}_2\text{SO}_4\text{-K}_2\text{CO}_3$ ). After removal of the ether, the residue was evacuated to 0.1 mm for 5 min. This residue in 21 mL of dimethyl sulfoxide was added dropwise to 1.76 g (26.6 mmol) of powdered potassium [ $^{13}\text{C}$ ]cyanide (Prochem, 91%  $^{13}\text{C}$ ) in 18 mL of dimethyl sulfoxide held in a bath at 124–134 °C. The procedure is that of Friedman,<sup>83</sup> who used halides with potassium cyanide in DMSO. The bath was raised to 138–145 °C and stirring continued for 4 h. The mixture was then stirred at room temperature overnight. After addition to 95 mL of cold water and ether extraction, the extract was washed with water and dried ( $\text{Na}_2\text{SO}_4$ ). Distillation gave 2.53 g of IX, bp 87–89 °C (18 mm) containing a small immiscible droplet. Redrying in a benzene solution ( $\text{Na}_2\text{SO}_4$ ) and distillation gave 2.39 g (17 mmol, 65.1% over two steps), bp 85.5–87 °C (17 mm) still containing the immiscible droplet.

**1-Hydroxooctanal-1- $^{13}\text{C}$ - $d_{15}$  (X).** The procedure of Keely<sup>84</sup> was used. A solution of 18 mL (18 mmol) of diisobutylaluminum hydride (Aldrich, 1 M in toluene) in 35 mL of ether was added slowly to 2.13 g (15.1 mmol) of the above cyanide in 20 mL of ether while stirring in a bath at 22 °C. After 45 min at 22 °C, the solution was refluxed gently for 30 min. The chilled solution was decomposed with 1.6 mL of water in 25 mL of dioxane, 25 mL of water was added, and the solution was shaken with 160 mL of 1 N hydrochloric acid. After 15 min standing the acid treatment was repeated. The ether extract was washed with 2% aqueous sodium carbonate and water and dried ( $\text{MgSO}_4$ ). Distillation gave 1.68 g of X (11.7 mmol, 77.5%), bp 68–71 °C/(17 mm). About 13% of the starting cyanide (IX) was shown to be still present by  $^{13}\text{C}$  NMR. This mixture was used in the next step without further purification.

**2-Hydro-2-nonanol-2- $^{13}\text{C}$ - $d_{18}$  (XI).** A stir bar and 0.15 g of Mg were placed in a dried, argon-flushed flask. A rubber septum was placed on top of the flask, and 15 mL of ether, freshly distilled from LiAlH<sub>4</sub>, was added via syringe. The seal was broken on 5 g of  $\text{ICD}_3$  (Merck) and 0.4 mL was delivered dropwise with the syringe. The mixture was cooled in an ice bath after the reaction started and stirred for 25 min after all of the iodomethane was added. An additional 0.15 mL of the perdeuterioiodomethane was added, the reaction mixture was stirred for 5 min, and then 0.05 mL more of the iodomethane was added and stirred for 10 min, until all of the Mg was used. While the mixture was cooled in the ice bath, the aldehyde from the previous step was added dropwise over 25 min using the syringe and stirred for 30 min at room temperature. The reaction mixture was cooled and 1 mL of water and then 3 mL of 0.2 N HCl are added. The mixture was extracted with ether, washed

with aqueous sodium bisulfite and with water, and dried overnight ( $\text{Na}_2\text{SO}_4$ ); the ether was evaporated. Because of the small quantity of XI obtained (about 0.6 g), distillation was not attempted.

**2-Hydro-2-iodononane-2- $^{13}\text{C}$ - $d_{18}$  (XII).** The same procedure as given above for the 5-iodononane (III) and the iodoheneicosane (VII) was followed, using 0.37 g (12 mmol) of phosphorus and 1.54 g (6.1 mmol) of  $\text{I}_2$  in 15 mL of clean dry chloroform. No distillation was attempted and this material (XII) was used in the next step.

**2,2-Dihydroxooctane-2- $^{13}\text{C}$ - $d_{18}$  (XIII).** The same procedure described above for IV was followed, using 0.45 g (1.65 mmol) of the above iodo compound (XII) with 3.5 mL of 1 N lithium triethylborohydride in THF. Here again, no distillation was attempted, and the final yield was approximately 0.2 g (1.4 mmol, 82%) of compound XIII. To make the NMR sample, 0.1678 g of this material was weighed into a 12-mm NMR tube along with 2.1831 g of perdeuteriodiglyme, giving a sample composition of 7.74 mol %. The sample was subjected to five freeze-pump-thaw cycles and sealed under vacuum. The  $^{13}\text{C}$  spectrum reveals the expected 1:2:1 triplet with small peaks on the downfield side of each component in the triplet, also with intensity 1:2:1. These low-intensity lines are attributed to the presence of a proton adjacent to the  $^{13}\text{CH}_2$  group in some of the sample molecules, causing a small isotope shift. The amount of sample labeled in this way is difficult to determine owing to the broad line (5 Hz) and small shifts involved, but was less than 10%. There was no simple way to separate these isotopic isomers. Since the *minimum* proton-proton distance between protons on adjacent carbons is only 1.5 Å, this minor isotopic impurity does not significantly alter the relaxation results. Fortunately, in all relaxation experiments performed on this sample, the isotopically shifted lines track the unshifted major lines. The  $^{13}\text{C}$  spectrum also initially revealed a doublet with a temperature-dependent chemical shift due to the presence of unreacted iodononane (present to less than 10% of the labeled nonane). At 313 K the upfield component of the doublet overlapped the downfield component of the triplet. Accordingly, this sample was broken open and the nonane and diglyme were codistilled to eliminate the iodo impurity, then again placed in a 12 mm NMR tube, degassed as before, and sealed under vacuum. This sample was used for the relaxation studies.

**Registry No.** I, 98195-33-6; II, 98195-35-8; III, 98195-37-0; IV, 98195-30-3; V, 98195-34-7; VI, 98195-38-1; VII, 98195-40-5; VIII, 98195-32-5; IX, 98195-41-6; X, 98195-43-8; XI, 98195-44-9; XII, 98195-45-0; XIII, 98195-31-4;  $\text{H}^{13}\text{C}(\text{O})\text{OK}$ , 86967-49-9;  $\text{Ph}_3\text{CHBr}$ , 776-74-9;  $\text{PhCH}_2\text{Br}$ , 100-39-0;  $\text{CD}_3(\text{CD}_2)_3\text{Br}$ , 98195-36-9;  $\text{CD}_3(\text{CD}_2)_9\text{Br}$ , 98195-39-2; AgOTs, 16836-95-6;  $\text{CD}_3(\text{CD}_2)_6\text{Br}$ , 98195-42-7;  $\text{ICD}_3$ , 865-50-9.

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## Communications to the Editor

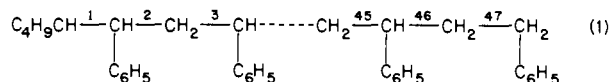
### Spontaneous Fragmentation of Cationic Polystyrene Chains

A. Grey Craig and Peter J. Derrick\*

*School of Chemistry, University of New South Wales  
Kensington, N.S.W., Australia*

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Using mass spectroscopic techniques, we have found that at low energies cationic polystyrene chains  $[\text{M}]^+$  (in the mass range 500–4500 units) fragment at bonds near the ends of chains. Bonds in the middle of the chains tend not to rupture. The effect is most pronounced with the longest chains. This preference for fragmentation near the ends of chains is proposed to be a consequence of stabilization of larger fragment ions due to charge delocalization. Polybutadiene  $[\text{M}]^+$ , polyethylene glycol  $[\text{M} + \text{H}]^+$ , and polypropylene glycol  $[\text{M} + \text{H}]^+$  cations behave similarly.<sup>1</sup>



Polystyrene molecular ions  $[\text{M}]^+$  were formed by field desorption,<sup>2-4</sup> and their fragmentation studied by mass-analyzed ion kinetic energy (MIKE) spectroscopy.<sup>5,6</sup> The MIKE spectrum of a given  $[\text{M}]^+$  was observed above a characteristic emitter

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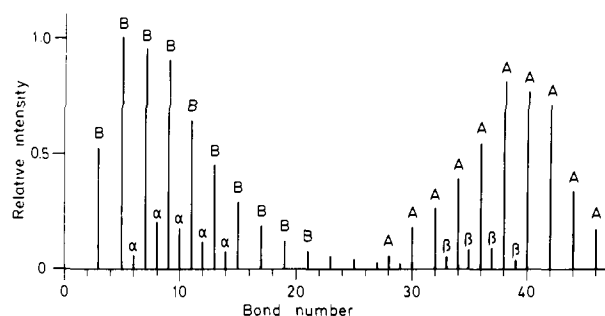
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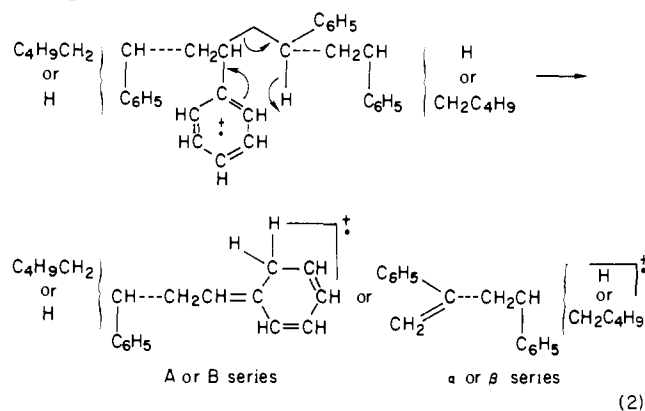
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**Figure 1.** Fragment ion intensities in the MIKE spectrum of the  $m/z$  2556.6  $[M]^+$  ion plotted against the bond numbers of the backbone bonds broken in their formation.

heating current (ehc),<sup>7</sup> disappeared if the ehc was lowered below that threshold, and reappeared if the ehc was raised again. Thresholds were higher for  $[M]^+$  ions of higher masses.<sup>8</sup> Above threshold, MIKE spectra were not sensitive to ehc. Peak intensities in the MIKE spectrum of the  $m/z$  2556.6  $[M]^+$  ion are plotted against the bond numbers [see (1)] of the ruptured bonds (Figure 1). The peaks fall into four series (A, B,  $\alpha$ , and  $\beta$ ) with nominal masses given by  $m_A = n104 + 58$ ,  $m_B = n104 + 92$ ,  $m_\alpha = n104$ , and  $m_\beta = n104 + 70$ . Mechanism 2 accounts for all four series of fragment ions.



The effects of ehc on the MIKE spectra indicate that the internal energy  $E$  of an  $[M]^+$  ion stems from thermal energy of its neutral precursor.<sup>10</sup> The thresholds are taken to be the ehc's above which there are detectable numbers of  $[M]^+$  ions possessing internal energy  $E$  appropriate for decomposition within the experimental time window (20–200  $\mu$ s). The shift of the threshold to higher ehc as the masses of the  $[M]^+$  ions increase is attributed to the slower rise of the rate constant  $k(E)$  with  $E$  as the number of internal degrees of freedom increases,<sup>11</sup> i.e., a kinetic effect akin to kinetic shift.<sup>12</sup>

Consider the B series of fragment ions and compare rupture at bond 5 with rupture at bond 25 in the  $m/z$  2556.6  $[M]^+$  ion. The fragment ion from rupture at bond 5 is the longer of the two fragment ions by 10 repeat units, and the neutral product from

rupture at bond 5 is the shorter of the two neutrals by the same amount. The fragment ion from rupture at bond 5 will, therefore, have a lower heat of formation than the fragment ion from rupture at bond 25, whereas the neutral from rupture at bond 5 will have a higher heat of formation than its counterpart from rupture at bond 25. We propose that, because of charge delocalization, the heats of formation of the ions depend more strongly upon size than the heats of formation of the neutrals.<sup>13</sup> In which case, the difference between the heats of formation of the two fragment ions will be greater than the difference between the heats of formation of the two neutral products, and the sum of the heats of formation of the products of bond-5 rupture must be lower than that of the products of bond-25 rupture. We propose that it is this difference in the values of the combined heats of formation of products, reflected in a difference in the critical energies, which is responsible for the fragment ion from bond-5 rupture being much more intense than that from bond-25 rupture.<sup>14,15</sup> The reversal in the pattern of charge retention ( $\beta$  series replacing B series, for example), once the midpoint of the  $[M]^+$  chain is passed, supports our proposal that the size of the ionic fragment is the factor directing fragmentation. RRKM calculations<sup>11a,12c</sup> indicate that an energy difference of about 10 kJ mol<sup>-1</sup> could account for this observed difference in intensities, provided the critical energies for decomposition did not exceed about 100 kJ mol<sup>-1</sup>. The hypothesis proposed implies that the charge is effectively delocalized in the polystyrene  $[M]^+$  ion, since ionization could occur at any of the aromatic nuclei.

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**Registry No.** Polystyrene radical cation, 76582-08-6.

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(14) The argument extends to fragment ions between bonds 5 and 29 and to the other series. The reduced intensity of bond-3 and absence of bond-1 fragment ions are attributed to high heats of formation of small neutrals.

(15) Expressed differently, rupture at bond 5 is favored because the ionization energy of the neutral precursor  $C_7H_7(CH_2CH(C_6H_5))_1H$  of the bond-5 fragment ion is lower than that of the neutral precursor  $C_7H_7(CH_2CH(C_6H_5))_{11}H$  of the bond-25 fragment ion, cf. Stevenson's rule.<sup>12</sup>

### Photoinduced $\alpha$ -Hydrogen Elimination of an Iridium(III) Dialkyl: Formation of an Isolable Iridium Methylidene

Michael D. Fryzuk,<sup>\*1</sup> Patricia A. MacNeil, and Steven J. Rettig<sup>2</sup>

Department of Chemistry  
University of British Columbia  
Vancouver, B.C., Canada V6T 1Y6

Received June 24, 1985

Although  $\alpha$ -elimination from transition-metal alkyls<sup>3</sup> might be expected to be a general route to alkylidene derivatives,<sup>4</sup> such reactivity has only been well documented for the early metals.<sup>5</sup> In fact, there are only two reports of  $\alpha$ -elimination involving a group 8–10 metal alkyl: the isolation<sup>6</sup> of  $[Ir=C(CH_2CH_2P(t-$

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