

deduced from molecular weight measurements, but this does not affect their conclusions. We have repeated the osmometry experiments of these authors and obtain essentially the same molecular weights. We have no ready explanation of this disagreement with the nmr results but consider the latter to be the more direct and less ambiguous method.

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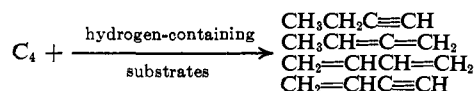
### Some Reactions of the C<sub>4</sub> Molecule

Sir:

The C<sub>4</sub> molecule has been recognized as a minor constituent of carbon vapor.<sup>1-9</sup> We are not aware of any previous report on its chemical interaction with other substances.

butatriene and 2-butyne, were not detected;<sup>11</sup> diacetylene, C<sub>4</sub>H<sub>2</sub>, was found in trace quantities only.

The hydrogenation of C<sub>4</sub> is analogous to the hydrogenation of C<sub>2</sub><sup>12</sup> and excited state C<sub>3</sub>.<sup>13</sup> The high-



dilution conditions of these experiments make unlikely the formation of these hydrocarbons by couplings of C<sub>2</sub> or C<sub>3</sub> radicals.

Preparations of the C<sub>4</sub> hydrocarbons employing <sup>14</sup>C-enriched graphite electrodes<sup>12</sup> confirm the electrodes as the sole source of their carbon skeleton; their relative molar activities are four times the activity of a product resulting from reaction of C<sub>1</sub>, by addition, with two molecules of alcoholic substrate (Table II).

The C<sub>4</sub> hydrocarbons from carbon vapor and C<sub>2</sub>D<sub>5</sub>-OH are 60-75% d<sub>5</sub> and d<sub>6</sub>, from CH<sub>3</sub>CD<sub>2</sub>OH, 80-85% d<sub>0</sub>, d<sub>1</sub>, and d<sub>2</sub>. Thus the substrates are the sources of the hydrogen atoms. The C<sub>4</sub> hydrocarbons are not formed from substrates which have rather high bond dissociation energies for removal of a hydrogen atom, such as water, benzene, and chlorobenzene.

The C<sub>4</sub> from a carbon arc produces these hydrocarbons; carbon vapor from thermal vaporization (re-

Table I. Reactions of C<sub>4</sub> with Selected Substrates

Product	Weight % of total carbon vaporized							
	Hexane	<i>cis</i> -2-Pentene	<i>t</i> -Butyl chloride	Methanol	Ethanol	1-Propanol	2-Propanol	<i>t</i> -Butyl alcohol
Ethylacetylene	0.61	0.24	0.13	0.30	0.34	1.10	0.54	1.02
Methylallene	0.18	0.08	0.35	0.28	0.34	0.65	0.60	0.61
1,3-Butadiene	0.20	0.55	0.71	0.03	0.05	0.71	0.18	0.72
Vinylacetylene	0.20	<i>a</i>	0.13	0.09	0.11	0.16	0.11	Nil
Total	1.19	0.87	1.32	0.70	0.84	2.62	1.43	2.35

<sup>a</sup> Not detectable in large quantities of *cis*-2-pentene by the isolation technique employed.

Simultaneous depositions of carbon vapor, from a high-vacuum arc,<sup>10</sup> and a variety of hydrogen-containing substrates (>1000-fold molar excess) on a liquid nitrogen cooled surface produce the C<sub>4</sub> hydrocarbons ethylacetylene, methylallene, 1,3-butadiene, and vinylacetylene (Table I). The total yields are similar and small, 1-2%, but the relative yields vary. Very small amounts of more highly hydrogenated C<sub>4</sub> hydrocarbons could be recognized with sensitive glpc detection systems, but the other C<sub>4</sub>H<sub>4</sub> and C<sub>4</sub>H<sub>6</sub> acyclics, 1,2,3-

Table II. Relative Molar Activities of C<sub>4</sub> Hydrocarbons Produced by the Reactions of <sup>14</sup>C-Enriched Carbon Vapor with Methanol and Ethanol

Product	Relative molar activities	
	Methanol	Ethanol
C <sub>1</sub> product, <sup>12</sup> CH <sub>2</sub> (OR) <sub>2</sub>	1.00	1.00
Ethylacetylene	4.12	4.02
Methylallene	4.00	3.86
Vinylacetylene	3.75	3.89
1,3-Butadiene	<i>a</i>	<i>a</i>

<sup>a</sup> Produced in insufficient quantity for accurate measurement.

sistive heating of a carbon filament) deposited on a -196° ethanol surface does not produce them. It is not clear at this time whether thermal vaporization (1) produces much less C<sub>4</sub> than arc vaporization or (2)

(11) 1,2,3-Butatriene would not be expected to survive the detection conditions: (a) W. M. Schubert, T. H. Liddicoet, and W. A. Lanka, *ibid.*, 76, 1929 (1954); (b) S. J. Cyvin, *Acta Chem. Scand.*, 17, 2123 (1963); (c) S. G. Frankiss and I. Matsubara, *J. Phys. Chem.*, 70, 1543 (1966).

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that excited state  $C_4$  is the hydrocarbon precursor. In analogous experiments with  $C_3$  it has been demonstrated that hydrogen abstraction is a property of excited state  $C_3$  only.<sup>13</sup> The design of the reactor,  $\sim 8$ -cm separation of generating and reacting zones, requires  $\sim 10^{-5}$  sec for the transit, thus limiting observations to excited states with radiative lifetimes in excess of this value.

The detailed mechanisms by which these multiple hydrogen transfers occur cannot be specified at this time.

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### Poly[tris(dialkylphosphinato)alanes]. Novel Tris(phosphinates) of Aluminum

Sir:

We wish to describe novel polymeric tris(phosphinates) of aluminum<sup>1</sup> which are soluble, fusible, and tractable. These poly[tris(dialkylphosphinato)alanes] are noteworthy for their high molecular weights and exceptionally high intrinsic viscosities.

Poly[tris(phosphinato)alanes], like other metal phosphinates,<sup>2–5</sup> form the most tractable polymers when prepared from unsymmetrical acids and mixtures of acids. Poly{bis[*n*-butyl(benzyl)phosphinato]di-*n*-octylphosphinatoalane},  $\{[C_4H_9(C_6H_5CH_2)PO_2]_2Al[O_2P(C_8H_{17})_2]\}_n$  (I), was prepared by the reaction of etherated alane,  $AlH_3 \cdot 0.3[(C_2H_5)_2O]$ , with a 2:1 mole ratio of *n*-butyl(benzyl)phosphinic and di-*n*-octylphosphinic acids in tetrahydrofuran (THF) at Dry Ice temperature. Evolution of hydrogen indicated a fast reaction at  $-70^\circ$ . Upon warming to ambient temperature, a clear, viscous solution was obtained. Samples were taken for analyses, and the solution (2.16 mg of polymer/ml) was heated under reflux for 4 hr. After sampling again, the polymer was isolated by evaporating the solvent under reduced pressure. A clear, colorless, coherent film formed on the reaction vessel wall. This film was non-solvated, semiflexible, hydrolytically stable, and resistant to swelling by common solvents.<sup>6</sup>

*Anal.* Calcd for  $C_{38}H_{66}AlO_6P_3$ : C, 61.77; H, 9.01; Al, 3.65. Found: C, 61.15; H, 9.04; Al, 3.03.

Analyses of the solutions indicated that the polymer increased in molecular weight<sup>7</sup> from 440,000 ( $n \approx 590$ ) to 460,000 ( $n \approx 620$ ) when heated for 4 hr. After 4 months at ambient temperature, the molecular weight

(1) General preparations of poly(phosphinatoalanes) were reported by D. L. Schmidt and E. E. Flagg at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract O-122.

(2) A. J. Sarceno and B. P. Block, *Inorg. Chem.*, **3**, 1699 (1964).

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(4) F. Giordano, L. Randaccio, and A. Ripamonti, *Chem. Commun.*, 1239 (1967).

(5) G. H. Dahl and B. P. Block, *Inorg. Chem.*, **6**, 1439 (1967).

(6) Before the solvent is completely removed, the solid polymer can be redissolved by adding more solvent and heating gently. In the non-solvated state, it is essentially insoluble in THF.

(7) Molecular weight determinations were made with a Mechrolab membrane osmometer; the reported values were obtained by extrapolation to infinite dilution.

increased to 780,000 ( $n \approx 1050$ ). Some polymer gradually precipitated from solution during the next 4 months. Gel permeation chromatography (gpc) was not applicable because the high viscosity interfered with the normal equilibration in the gpc columns, and further dilution prevented proper detection by the index of refraction method. X-Ray powder patterns confirmed that the polymer was crystalline before and after melting ( $315^\circ$ ). A thermogravimetric analysis ( $N_2$ ,  $10^\circ/\text{min}$ ) indicated that rapid decomposition began at  $400^\circ$ .

Poly{bis[*n*-butyl(benzyl)phosphinato]di-*n*-heptylphosphinatoalane},  $\{[C_4H_9(C_6H_5CH_2)PO_2]_2Al[O_2P(C_7H_{15})_2]\}_n$  (II), was prepared by the same procedure as I and gave similar properties. Molecular weight determinations gave approximate values between 200,000 and 500,000 ( $n \approx 270$ –670). This colorless, crystalline polymer was semiflexible and formed clear, coherent films. The polymer melted near  $295^\circ$  and rapid decomposition began at  $400^\circ$ .

*Anal.* Calcd for  $C_{36}H_{62}AlO_6P_3$ : C, 60.8; H, 8.79; Al, 3.80. Found: C, 60.9; H, 8.77; Al, 3.67.

An unusually high intrinsic viscosity of 37 dl/g (THF,  $25^\circ$ ) was measured<sup>8</sup> for polymer I, and the viscosity of polymer II was comparable. Intrinsic viscosities of this magnitude are observed for polyelectrolytes,<sup>9</sup> but this value is much larger than those reported for other metal phosphinates. It suggests that these poly[tris(phosphinato)alanes] form partially rigid, rodlike molecules with large effective hydrodynamic volumes in solution. Thus, the alkyl groups form an effective organic layer around the inorganic skeletal structure and contribute significantly to the over-all properties.

The following structural features should be considered: (1) interchain phosphinato bridging or three-dimensional networks; (2) phosphinato moieties coordinated to the same or different aluminum(III) ions in a molecule; (3) free phosphinato moieties and phosphinato bridges; or (4) predominantly tris(phosphinato) bridging between adjacent monomer units. If interchain bridging or three-dimensional networks were extensive, polymers I and II would be intractable. It seems probable that less tractable systems such as poly[tris(diphenylphosphinato)alane] fall in this category.<sup>10,11</sup> It should be noted that insoluble, coherent films of chromium(III) tris(phosphinates)<sup>12</sup> have been prepared which apparently do not consist of three-dimensional networks.

Infrared spectral data indicate that the phosphinato P–O bonds are approximately equivalent. No characteristic phosphoryl bands are observed near  $1200\text{ cm}^{-1}$ . If there are free phosphinato moieties, they constitute a small fraction of the total.

If the phosphinato moieties coordinate to the same aluminum ion, chain termination can take place. The fact that the polymers continue to grow in solution suggests that this type of coordination is not favored.

(8) Standard techniques were used; see F. W. Billmeyer, "Textbook of Polymer Science," Interscience Publishers, New York, N. Y., 1966, pp 53–87.

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