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.[13] The design of the reactor, ~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[1] 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,[2–5] 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°. 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 nonsolvated, semiflexible, hydrolytically stable, and resistant to swelling by common solvents.[6]

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[7] 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 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°). A thermogravimetric analysis (N_2, 10°/min) indicated that rapid decomposition began at 400°.

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° and rapid decomposition began at 400°.

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°) was measured[8] for polymer I, and the viscosity of polymer II was comparable. Intrinsic viscosities of this magnitude are observed for polyelectrolytes,[9] 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.[10,11] It should be noted that insoluble, coherent films of chromium(III) tris(phosphinates)[12] 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 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.

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(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).

(3) S. H. Rose and B. P. Block, *J. Am. Chem. Soc.*, 87, 2076 (1965).

(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 nonsolvated 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.

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

(9) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 489–512.

(10) R. A. Sutton and J. Wood, British Patent 1,018,456 (1966); *Chem. Abstr.*, 64, 17748*f* (1966).

(11) J. J. Pitts, M. A. Robinson, and S. I. Trotz, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstract L-80.

(12) A. J. Saraceno, J. P. King, and B. P. Block, *J. Polymer Sci., Part B*, 6, 15 (1968).

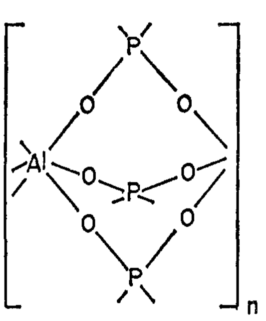

Figure 1. Postulated structure of the poly[tris(phosphinato)-alanes] (in solution with alkyl groups deleted).

Structural data for other metal phosphinates support this conclusion.[13,14]

From available data, we conclude that the predominant structural feature is repeating units of tris(phosphinato) triple bridges. The aluminum(III) ion is therefore in a six-coordinate octahedral configuration (Figure 1). This postulated structure is consistent with rigid, rodlike polymer chains in solution. A study has been initiated to determine the solid-state structures by X-ray fiber photography, but the results are too preliminary to report at this time.

Acknowledgment. This work was supported in part by the Office of Naval Research.

[13] V. Giancotti, F. Giordano, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.*, *A*, 757 (1968).

[14] F. Gemiti, V. Giancotti, and A. Ripamonti, *ibid.*, 763 (1968).

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The Relationship between Isotope Effects and Reactivity[1]

Sir:

Isotope effect theory predicts that the magnitude of primary hydrogen isotope effects on reaction rates will vary smoothly and pass through a maximum value as transition-state symmetry is changed in a regular way.[2] Such behavior has been observed for a series of isotope effects on base-catalyzed proton removal from carbon when the comparison is made in terms of differences in basicity between the proton donor and the proton acceptor (ΔpK_a);[3] this suggests that the latter quantity is a good measure of transition-state symmetry. These isotope effects, however, do not correlate at all well with the rates of these reactions,[3a] despite the fact that relative reactivities are a popularly employed measure of transition-state structure.[4] We wish here to present some new data which, when coupled with other measurements, indicate the circumstances under which relative reactivity can correlate the magnitude of isotope effects and, by implication, serve to measure transition-state symmetry.

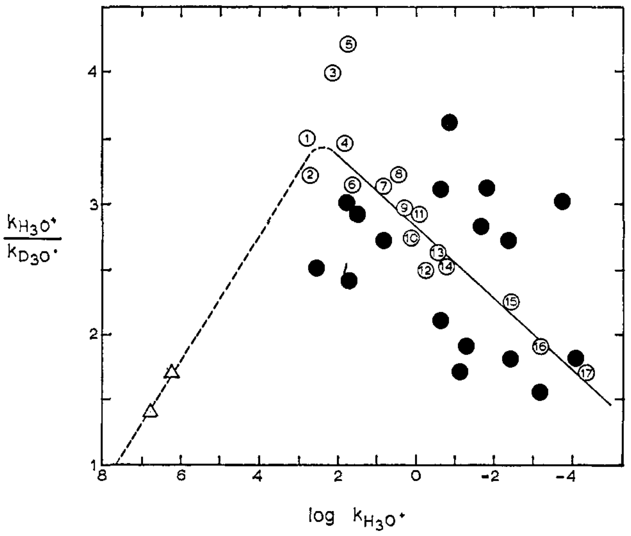

Figure 1. Relationship between $k_{H_3O^+}/k_{D_3O^+}$ and log $k_{H_3O^+}$ for rate-determining proton-transfer reactions. Open circles represent hydrolysis of the following vinyl ethers: (1) ethyl isopropenyl ether, (2) ethyl cyclopentenyl ether, (3) ethyl α-phenylvinyl ether, (4) ethyl cyclohexenyl ether, (5) methyl α-phenylvinyl ether, (6) methyl cyclohexenyl ether, (7) phenyl isopropenyl ether, (8) α-naphthyl isopropenyl ether, (9) ethyl vinyl ether,[7c] (10) isopropyl *cis*-propenyl ether, (11) methyl vinyl ether, (12) ethyl *cis*-propenyl ether, (13) methyl *cis*-propenyl ether, (14) β-chloroethyl vinyl ether,[7b] (15) phenyl vinyl ether, (16) *m*-bromophenyl vinyl ether, (17) 2,5-dimethylfuran.[7a]

We have determined the isotope effect, $k_{H_3O^+}/k_{D_3O^+}$, on the hydrolysis of 14 vinyl ethers in wholly aqueous solution at 25°.[5] These, together with three other examples for the same reaction reported in the literature,[7] increase regularly with log $k_{H_3O^+}$ up to a value of $\sim$3.5 (Figure 1, open circles). Inclusion of two isotope effects on a closely similar reaction, proton transfer to the α carbon of enolate anions (Figure 1, triangles),[8] suggests, in accordance with theory,[9,11] that this is the maximum normal value of this isotope effect and that the two reactions showing high values of $k_{H_3O^+}/k_{D_3O^+}$ may be experiencing tunnel effects.[3a] When similar isotope effects on other rate-determining proton-transfer reactions are added, however, this correlation is destroyed (Figure 1, filled circles.)[12]

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[1] This research was supported by a grant (GP 6580) from the National Science Foundation.

[2] See R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc.*, *B*, 985 (1967), for a recent review and references to previous literature.

[3] (a) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.* (London), **A294**, 273 (1966); (b) J. L. Longridge and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1292 (1967).

[4] G. Hammond, *ibid.*, **77**, 334 (1955); E. R. Thornton, *ibid.*, **89**, 2915 (1967).

[5] Standard criteria[6] were used to show that proton transfer from H_3O^+ is rate determining in each of these reactions.

[6] A. J. Kresge and Y. Chiang, *J. Chem. Soc.*, *B*, 53 (1967).

[7] (a) E. J. Stamhuis, W. Drenth, and H. van den Berg, *Rec. Trav. Chim.*, **83**, 167 (1964); (b) P. Saloma, A. Kankaanpera, and M. Lajunen, *Acta Chem. Scand.*, **20**, 1790 (1966); (c) A. J. Kresge and Y. Chiang, *J. Chem. Soc.*, *B*, 58 (1967).

[8] F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958); T. Riley and F. A. Long, *J. Am. Chem. Soc.*, **84**, 522 (1962).

[9] The rate ratio $k_{H_3O^+}/k_{D_3O^+}$ contains an inverse secondary isotope effect[10] in addition to the normal primary effect; it has been estimated[11] that the former will serve to reduce the over-all isotope effect to approximately half the expected value for simple oxygen–hydrogen bond breaking.

[10] A. J. Kresge and D. P. Onwood, *J. Am. Chem. Soc.*, **86**, 5014 (1964); M. M. Kreevoy, P. W. Steinwand, and W. Y. Kayser, *ibid.*, **86**, 5013 (1964).

[11] C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42, 3207, 3214 (1961); C. G. Swain and E. R. Thornton, *ibid.*, **83**, 3884 (1961).

[12] These additional values are restricted to isotope effects which can be identified as $k_{H_3O^+}/k_{D_3O^+}$ measured in dilute, wholly aqueous solution at 25°. They include the acid cleavage of mercurials (vinylmercuric iodide,[13] allylmercuric iodide,[14] and 2,4-dimethoxyphenylmercuric chloride[15]), 2,4-dimethoxybenzeneboronic acid,[16] and tetraphenylborate ion;[17] the hydration of carbon–carbon double bonds (isobutylene,[18] 1-