J. Am. Chem. Soc. **1981**, *103*, 5248-5249

Kinetics of an Intraresin Reaction[1]

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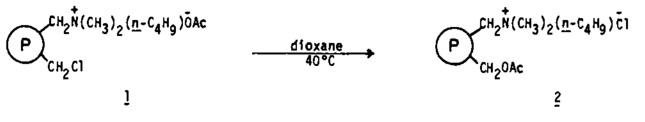
Received April 10, 1981

The study of "site–site interactions" in cross-linked polymers has attracted considerable interest over the past 10 years.[2] Surprisingly, however, very little attention has focused on the *rates* of such processes.[3] In this communication we report the kinetics of the intraresin conversion of **1** to **2**. Data presented below provide compelling evidence that (1) polymer-bound acetate reacts as an ion pair, (2) the encounter frequency of pendant groups is nonuniform, and (3) 30% of the pendant groups in **1** become "kinetically isolated".



1 2

cross-linked polystyrene gel--
1% divinylbenzene (200-400 mesh)

0.59 mmol $\bar{O}Ac$/g
0.59 mmol Cl/g

Reaction of chloromethylated polystyrene (10.0 g, 1.54 mmol of Cl/g) with 0.5 equiv of *N*,*N*-dimethyl-*n*-butylamine in toluene (55 mL) for 48 h at 100 °C resulted in complete quaternization of the amine.[4] Acetate was exchanged for ionic chloride by stirring 3.0 g of the polymer with a mixture of 15 mL of toluene, 3 mL of glacial acetic acid, and 15 mL of a saturated aqueous sodium acetate solution for 3 h at 22 °C. The resulting resin (**1**), was (1) washed sequentially with 2 × 10 mL of distilled water, 5 × 10 mL of 50% dioxane–water (v/v), and 5 × 10 mL of dioxane, (2) divided into 1.0-g samples (dioxane swollen), and (3) suspended in 5 mL of dioxane maintained at 40 °C.[6,7] Intraresin displacement was monitored by using a one vial, one kinetic point technique by withdrawing appropriate samples and analyzing for ionic chloride.[5] Swelling was constant throughout the entire reaction.[8] In order to ensure that trace ionic impurities did not generate soluble acetate, a "three-phase test" was carried out.[9] Chloromethylated polystyrene was fully quaternized with *N*,*N*-dimethyl-*n*-butylamine and exchanged with acetate by using procedures similar to those described above. The polymer was then mixed with a portion of chloromethylated polystyrene and heated in dioxane for 24 h at 40 °C. Analysis showed that no ionic chloride was formed.

A second-order plot of the data is presented in Figure 1. In the range of 0–70% conversion, good linearity is observed. If the initial effective concentration of reactants is assumed to be 0.16 M, the specific rate constant is 3.7×10^{-4} L mol^{-1} s^{-1}.[10,11] This value compares reasonably well with the second-order rate constant for the reaction of benzyl chloride with benzyl-*N*,*N*-dimethyl-*n*-butylammonium acetate in dioxane at 40 °C ($k = 12.1 \times 10^{-4}$ L mol^{-1} s^{-1}).[12] The apparent activation energy for both polymer and solution processes is 13 kcal mol^{-1}.[13] Unlike the homogeneous reaction, the polymeric displacement exhibited a significant decrease in rate after 70% conversion. In order to establish that the remaining chloromethylene and acetate groups were active for displacement, 0.20-g samples of **2** (72% conversion) were reacted separately with 5 mL of 0.05 M benzyl chloride and 5 mL of 0.05 M benzyl-*N*,*N*-dimethyl-*n*-butylammonium acetate at 40 °C.[14] In both cases the total yield of chloride ion, based on the polymeric reactant, increased to 90% after 2 h.

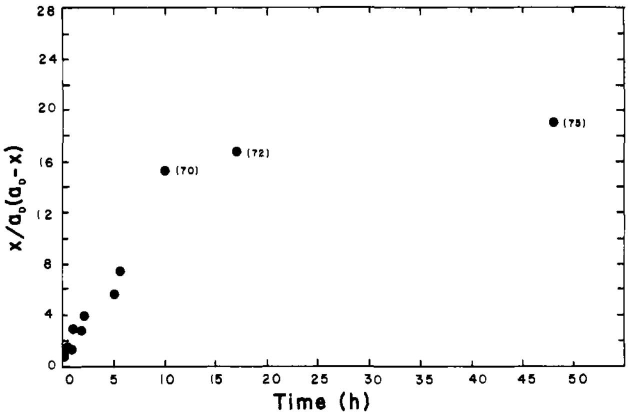


Figure 1. Plot of $x/[a_0(a_0 - x)]$ as a function of time for the conversion of **1** to **2** at 40 °C. x = chloride ion concentration (M); a_0 = initial concentration (M) of pendant quaternary ammonium and chloromethylene groups. Numbers in parentheses indicate the percent conversion.

Quaternary ammonium salts exist almost exclusively as ion pairs in dioxane.[15] On the basis of correlations made between cation–anion interaction energies and S_N2 reactivity, convincing arguments have been made which suggest that these salts react in the form of ion pairs.[15,16] The present results substantially strengthen this view by showing that pendant acetate and chloromethylene groups become "kinetically isolated" with respect to each other but react readily with soluble analogues. The similarity in rate between the solution and the initial polymeric displacement indicates that the resinous reactants encounter one another at rates equal to or greater than the rate of chemical reaction. Beyond 70% conversion, however, chain dynamics and/or conformation control the observed kinetics and site–site encounters occur with half-lives greater than 4.7 h.[17] These results clearly demonstrate that a gradation of encounter frequencies exists.[18]

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(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

(2) For recent reviews, see: Kraus, M. A.; Patchornik, A. *Macromol. Rev.* **1980**, *15*, 55. Kraus, M. A.; Patchornik, A. *Isr. J. Chem.* **1978**, *17*, 298. Crowley, J. I.; Rapoport, H. *Acc. Chem. Res.* **1976**, 135. Hodge, P.; Sherrington, D. C. "Polymer-Supported Reactions in Organic Synthesis"; Wiley: New York, 1980. Mathur, N. K.; Narang, C. K.; Williams, R. E. "Polymers as Aids in Organic Chemistry"; Academic Press: New York, 1980.

(3) From delayed trapping experiments, the encounter frequency of pendant groups on lightly cross-linked polystyrene has recently been estimated to be on the order of 10^{-2}–10^{-3} s^{-1} (Mazur, S.; Jayalekshmy, P. *J. Am. Chem. Soc.* **1979**, *101*, 677. Rebek, J., Jr.; Trend, J. E. *Ibid.* **1979**, *101*, 737).

(4) The polymer was washed extensively with toluene, dried [100 °C, 5 h (0.1 mm)], and analyzed for chloride ion by treating a portion with nitric acid and then performing a modified Volhard titration;[5] the ionic chloride content was 0.61 mmol/g. The total chlorine present was 1.22 mequiv/g.

(5) Stewart, J. M.; Young, J. D. "Solid Phase Peptide Synthesis"; W. H. Freeman; San Francisco, CA, 1969; p 55.

(6) Dioxane was dried by distillation from sodium benzophenone ketyl.

(7) The total time spent for the final dioxane washing, weighing of individual samples, and beginning the kinetic run was ca. 15 min. Using this procedure, ion exchange was complete and intraresin reaction was negligible as evidenced by analysis of **1** for ionic and covalent chloride, plus analysis of the filtrate for chloride ion.

(8) Imbibed dioxane equalled 2.75 g/g of dry polymer.

(9) For a description of the "three-phase test", see: Rebek, J.; Gavina, F. *J. Am. Chem. Soc.* **1975**, *97*, 3453.

(10) Chloromethylated polystyrene was derived from copolymerization of styrene, vinylbenzyl chloride, and divinylbenzene in order to ensure an approximately random distribution of chloromethylene groups throughout the bead. The additional fact that quaternization of the polymer using a 10-fold excess of *N*,*N*-dimethyl-*n*-butylamine in toluene at 40 °C obeys clean pseudo-first-order kinetics over 90% conversion indicates uniform reactivity of the chloromethylene groups. Since a minimum volume of toluene was used for swelling in the preparation of **1**, and >95% of the toluene solution of amine was *within* the beads, quaternization must be close to random.

(11) Initial effective concentration = (0.59 mmol reactant/g of dry resin)/[3.7 mL (imbibed solvent plus resin/g of dry resin)] = 0.16 M.

(12) Homogeneous reactions were carried out with equal concentrations of reactant (0.05 M) and were monitored by the appearance of chloride ion.

(13) Rate constants for homogeneous displacement at 40, 50, and 60 °C were 12.1×10^{-4}, 27.7×10^{-4}, and 44.9×10^{-4} L mol^{-1} s^{-1}, respectively. The second-order rate constants for the initial intraresin reaction at 20 and 60 °C were 0.66×10^{-4} and 9.7×10^{-4} L mol^{-1} s^{-1}.

(14) Under the reaction conditions used, absorption of benzyl chloride by **1** was negligible; benzyl-*N*,*N*-dimethyl-*n*-butylammonium acetate was absorbed to a small extent (0.25 mmol/g of dry polymer).

(15) Ugelstad, J.; Ellingsen, T.; Berge, A. *Acta Chem. Scand.* **1966**, *20*, 1593.

(16) Starks, C. M.; Liotta, C. L. "Phase Transfer Catalysis"; Academic Press: New York, 1978; p 31-37.

(17) Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 708.

0002-7863/81/1503-5248$01.25/0

The conversion of **1** to **2** represents the simplest intraresin reaction reported to date. It proceeds without a significant change in cross-link density and resin composition and is amenable to direct kinetic analysis. Further studies based on this system are in progress.

Acknowledgment. We are grateful to Dr. Stephen Mazur (E. I. du Pont de Nemours and Co.) for helpful discussions.

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(18) In principle, the extent of kinetic isolation in cross-linked polymers should depend upon the chemical rate and the distribution of encounter frequencies. While 30% of the sites in **1** become isolated, faster chemical reactions using similar supports should result in even greater isolation; slower reactions should yield fewer isolated sites.

Tris[phenyl(difluorophosphino)amino]phosphine ($P[N(C_6H_5)PF_2]_3$), a Novel Tridentate Strong π-Acceptor Ligand Forming Cage Chelates. Crystal Structure of the Chelate Complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$

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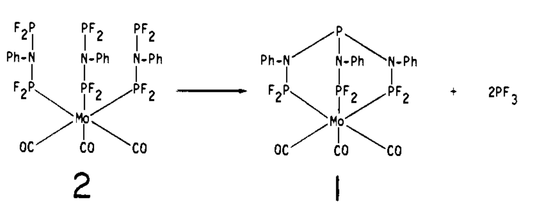
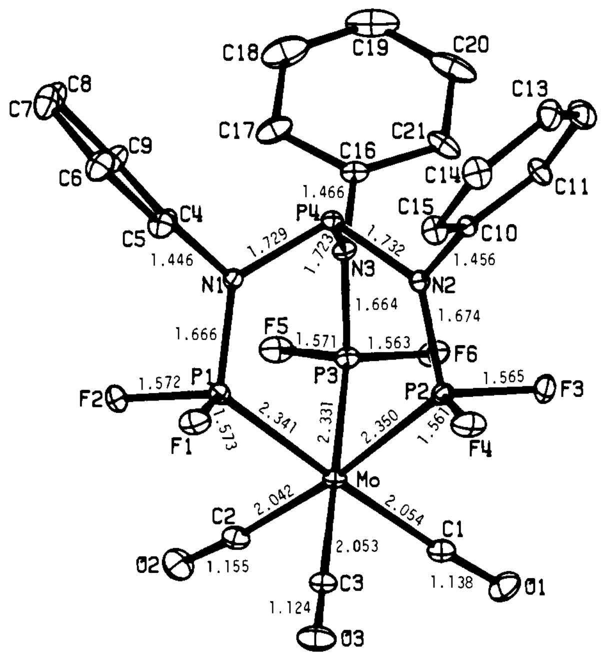
Received April 9, 1981
Revised Manuscript Received July 1, 1981

Chelating strong π-acceptor ligands are of interest in connection with the stabilization of complexes of transition metals in low oxidation states that exhibit unusual chemical properties,[2] including the important one of activity in homogeneous catalytic reactions. We report the first example of a tridentate chelating strong π-acceptor ligand containing three σ-donor, π-acceptor PF_2 groups and describe the novel bicyclo[2.2.2]octane-like cage structure of the complex $P[N(C_6H_5)PF_2]_3Mo(CO)_3$ (**1**) in which the ligand has been identified. The new tridentate ligand, tris[phenyl(difluorophosphino)amino]phosphine, is formed by an unprecedented reaction, the elimination of PF_3 from *N,N*-bis(difluorophosphino)aniline ($C_6H_5N(PF_2)_2$), which occurs when *fac*-$(CH_3CN)_3Mo(CO)_3$ reacts with the latter to yield **1** as an unexpected product. We suppose that the mechanism of formation of the ligand $P[N(C_6H_5)PF_2]_3$ involves an initial step in which $C_6H_5N(PF_2)_2$ reacts as a monodentate ligand with *fac*-$(CH_3CN)_3Mo(CO)_3$ to yield *fac*-$[C_6H_5N(PF_2)_2]_3Mo(CO)_3$ (**2**) by simple ligand substitution. Then the proximity of the three uncomplexed PF_2 groups of the three mutually cis $C_6H_5N(PF_2)_2$ ligands in **2**, coupled with the tendency to form six-membered chelate rings, facilitates the elimination of PF_3 to form the tridentate ligand in place in **1**.



A solution of *fac*-$(CH_3CN)_3Mo(CO)_3$ was generated by boiling 4.0 g (15 mmol) of $Mo(CO)_6$ in 75 mL of acetonitrile for 24 h. This solution was stirred with 5.0 g (22 mmol) of $C_6H_5N(PF_2)_2$[3] for 2 days at 40-45 °C. Solvent was then removed in vacuum, and the residue was extracted with pentane. Concentration and cooling of the pentane extract gave 1.0 g of a white crystalline metal carbonyl complex (**1**), mp 229-231 °C, sublimation temperature 125 °C (0.001 mm). Since the stoichiometry and structure of **1** could not be determined by conventional analytical and spectroscopic methods, the product was subjected to single-crystal X-ray diffraction analysis.



P1-Mo-P2	86.8(1)	P1-Mo-P3	88.5(1)	P2-Mo-P3	85.3(1)
C1-Mo-C2	93.9(3)	C1-Mo-C3	88.9(3)	C2-Mo-C3	92.1(3)
C1-Mo-P2	89.6(2)	C2-Mo-P1	89.7(2)	C3-Mo-P1	90.4(2)
C1-Mo-P3	92.1(2)	C2-Mo-P3	88.7(2)	C3-Mo-P2	93.9(2)
C1-Mo-P1	176.3(2)	C2-Mo-P2	173.2(2)	C3-Mo-P3	178.7(2)
Mo-C1-O1	176.6(6)	Mo-C2-O2	175.0(6)	Mo-C3-O3	178.5(6)
Mo-P1-N1	118.0(2)	Mo-P2-N2	117.1(2)	Mo-P3-N3	116.9(2)
Mo-P1-F1	117.6(2)	Mo-P2-F3	118.6(2)	Mo-P3-F5	120.5(2)
Mo-P1-F2	120.4(2)	Mo-P2-F4	120.9(2)	Mo-P3-F6	119.1(2)
N1-P1-F1	102.4(2)	N2-P2-F3	101.0(2)	N3-P3-F5	100.8(2)
N1-P1-F2	100.5(2)	N2-P2-F4	100.5(2)	N3-P3-F6	101.3(2)
F1-P1-F2	93.5(2)	F3-P2-F4	94.5(3)	F5-P3-F6	94.0(2)
N1-P4-N2	103.0(2)	N1-P4-N3	104.2(2)	N2-P4-N3	104.1(2)
P1-N1-P4	123.8(3)	P2-N2-P4	124.1(3)	P3-N3-P4	125.7(3)
P1-N1-C4	122.3(4)	P2-N2-C10	122.4(4)	P3-N3-C16	119.4(4)
P4-N1-C4	113.4(4)	P4-N2-C10	113.3(4)	P4-N3-C16	114.9(4)

Figure 1. The structure of $P[N(C_6H_5)PF_2]_3Mo(CO)_3$, showing all important bond lengths (Å) and valence angles (deg). The estimated standard deviations of the bond lengths are Mo-P, 0.002; Mo-C, 0.008; P-F, 0.004; P-N, 0.005; N-C, 0.007; C-O, 0.007 Å. The atoms are represented by their thermal ellipsoids of 10% probability.

The product **1** forms monoclinic crystals by slow evaporation of a diethyl ether solution. The space group is $P2_1/c$, uniquely determined by the systematic absences. From diffractometric data, the unit-cell parameters are $a = 8.683$ (1) Å, $b = 28.218$ (7) Å, $c = 15.338$ (2) Å, and $\beta = 118.12$ (1)°. There are four molecules per cell. The structure was determined from intensity data recorded with an automatic diffractometer using filtered Mo Kα radiation and the θ-2θ step-scan technique to the limit of $2\theta = 50°$. Absorption corrections were applied. The solution for the structure was obtained by the heavy-atom method, and refinement was done by the full-matrix least-squares method. Anisotropic thermal parameters were adjusted for all 38 nonhydrogen atoms of an asymmetric unit of formula $P[N(C_6H_5)PF_2]_3Mo(CO)_3$. The hydrogen atoms were not located. The final discrepancy index $R(F)$ is 0.052, on the basis of 3079 reflections having $F_{obsd}^2 > 2\sigma(F_{obsd}^2)$.

The structure of **1**, shown in Figure 1, is that of an octahedral *fac*-$L_3Mo(CO)_3$ complex. The tridentate ligand, $P[N(C_6H_5)PF_2]_3$, has its three PF_2 groups linked to the Mo atom so as to form a cage molecule with interlocking six-membered rings, similar to bicyclo[2.2.2]octane. As one of the bridgehead atoms of the cage, the central phosphorus atom of the tridentate ligand is not directly bonded to the Mo atom, which is the other bridgehead atom.

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[1] Visiting scientist from Department of Chemistry, Carleton College, Northfield, MN 55057.

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