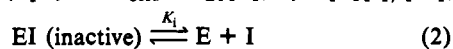


Figure 2. Plot of $1/k_{\text{obs}}$ (s) vs $[I]$ for $I = \text{SO}_4^{2-}$ (O) and Cl^- (Δ). Experiments were performed under the conditions described in Figure 1. Dissociation constants K_i are $0.8 (\pm 0.2)$ mM for SO_4^{2-} and $4 (\pm 1)$ mM for Cl^- and can be obtained from the x -intercepts of the plot.

concentrations were satisfactorily fit to a single exponential process.

The kinetic effects of anion binding can be explained by the formation of an inactive complex (EI) upon anion (I) binding (eq 2)¹⁶ that is incapable of undergoing intramolecular ET (eq 3). Free photoreduced enzyme (E) is generated by ligand dissociation from this complex (eq 2). If $k_{\text{obsd}} = k_{\text{ET}}[E]$, $K_i = [E][I]/[EI]$,



and k_{ET} is defined as the rate constant for intramolecular ET in the absence of anions,¹⁷ then substitution for $[E]$ using the expression for K_i gives

$$\frac{1}{k_{\text{obsd}}} = \frac{[I]}{K_i k_{\text{ET}}} + \frac{1}{k_{\text{ET}}} \quad (4)$$

Thus, a plot of $1/k_{\text{obsd}}$ vs $[I]$ will give a straight line with a slope of $1/K_i k_{\text{ET}}$ and an intercept of $1/k_{\text{ET}}$, as shown in Figure 2 for SO_4^{2-} and Cl^- .

These results verify that an anion binding site exists on sulfite oxidase and provide direct kinetic evidence that intramolecular ET is inhibited by anion binding. The structural basis for this effect is currently unknown because there is as yet no X-ray structural data available for sulfite oxidase (or any other pterin-containing molybdenum enzyme).¹⁸ The inhibition of sulfite oxidase turnover by anions under steady-state conditions may also be due to limitations on intramolecular ET because similar anion binding constants are obtained for both the steady-state¹⁰ and flash photolysis experiments. Previous evidence for similar kinetic effects in redox enzymes or metalloproteins comes from a lack of dependence of rates of ET on driving force,^{4c} the facilitation of ET upon the binding of a ligand,^{4e,f} and surface diffusion within electrostatic complexes.^{4g}

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(16) The ET rate of the inactive species need not be zero, but it must be smaller than the slowest rate observed at high salt concentration because all of the ET reactions can be satisfactorily fit by a single exponential.

(17) In these equations, E represents the Fe(II),Mo(VI) species created upon flash photolysis, and P the Fe(III),Mo(V) species resulting from intramolecular electron transfer. k_{ET} represents the sum of the forward and reverse rate constants for this process.

(18) See ref 3c for a discussion of the effect of distance on ET rates.

(19) Tris: tris(hydroxymethyl)aminomethane, $pK_a = 8.1$; Bis-Tris: [bis-(2-hydroxyethyl)amino]tris(hydroxymethyl)methane, $pK_a = 6.5$; Bis-tris propane: 1,3-bis[[tris(hydroxymethyl)methyl]amino]propane, $pK_{a1} = 6.8$, $pK_{a2} = 9.0$.

The Intrinsic Competition between Elimination and Substitution Mechanisms Is Controlled by Nucleophile Structure

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Whereas the competition between $\text{S}_{\text{N}}2$ and E2 mechanisms is among the best understood reactivity-selectivity relationships in the liquid phase,¹ the gas-phase anion-molecule counterpart²⁻¹⁰ is much less well defined. Gas-phase studies are hindered because the readily measured ionic product is identical for both mechanisms while the distinct neutral products are extremely difficult to detect. The difficulty of precisely controlling the interaction energy further complicates some gas-phase investigations. Recent FA-SIFT studies using localized heteroatomic bases with simple alkyl halides concluded that elimination is often kinetically favored over substitution.^{11,12} Substitution, however, is preferred for sulfur anions reacting with alkyl halides, and substitution effectively competes with elimination when the localized base H_2N^- reacts with ethyl methyl sulfite.¹³ We wish to report that the competition between elimination and substitution at simple alkyl centers depends, most importantly, on the type of base used rather than its thermodynamic basicity; localized heteroatomic bases prefer to react with ethyl dimethyl phosphate by elimination while delocalized carbon bases prefer substitution.

Ethyl dimethyl phosphate¹⁴ is an ideal substrate for these competition studies. First, it contains a common, excellent leaving group,¹⁵ $\Delta H_{\text{acid}}^{\circ}[(\text{RO})_2\text{POOH}] \approx 332 \text{ kcal mol}^{-1}$, for both substitution and elimination channels. Second, the competition of interest is "intramolecular", obviating the need to consider differences in ion-neutral dynamics or energetics when distinct substrates are used. Third, reaction at phosphorus is negligible¹⁵ while substitution and elimination reactions are facile. Fourth,

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Scheme I. Generalized Scheme for the Reactions of Anions with Ethyl Dimethyl Phosphate

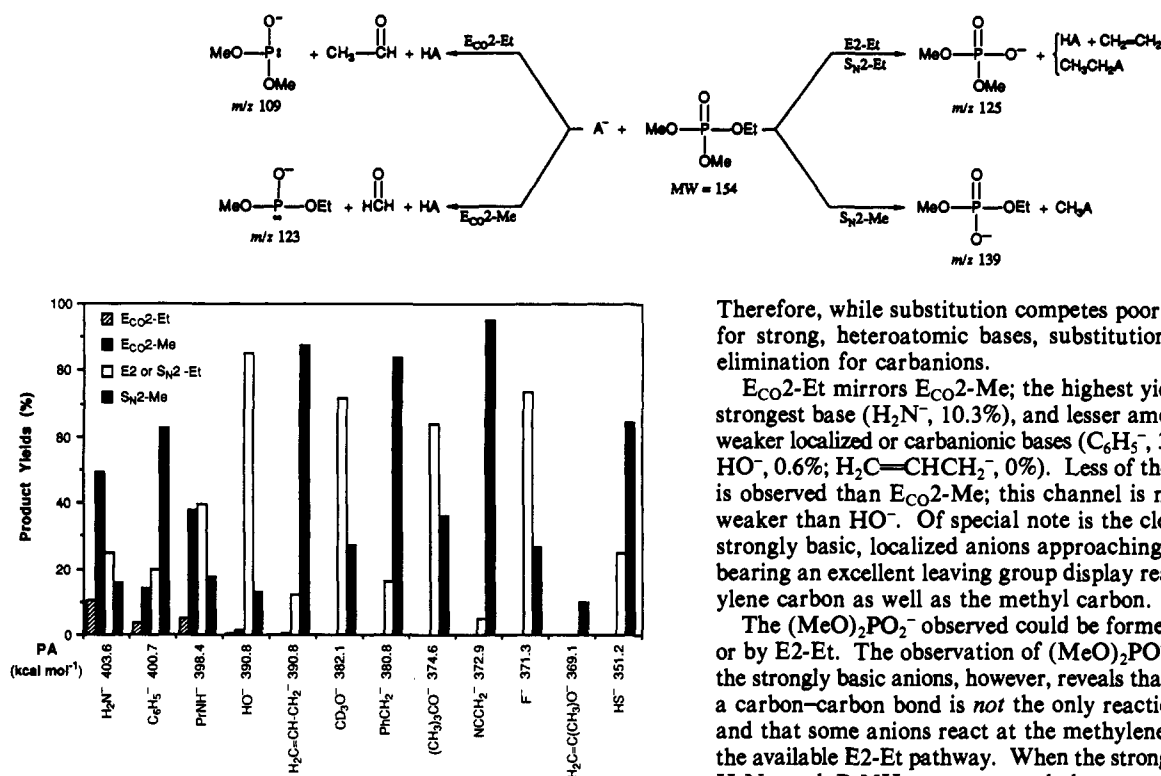


Figure 1. Product yields for the reaction of anions with ethyl dimethyl phosphate. The anions are listed in order of decreasing basicity (ref 16). The yields reported (the average of two independent measurements) have been corrected from the raw observed yields for all naturally occurring isotopes (refs 17 and 18) and for reaction due to a 2.7% impurity of ethyl methyl phosphate. CD₃O⁻ also produces 1.2% reaction at phosphorus; F⁻ also produces a trace ($\leq 0.6\%$) amount of reaction at phosphorus; H₂C=C(CH₃)O⁻ also produces 90.3% adduct/cluster formation; HS⁻ also produces 10.8% adduct/cluster formation. The ionic products assigned to each mechanistic path are noted in Scheme I.

the products from reaction at methyl versus ethyl are distinguishable; therefore, observed product yields directly reflect the mechanistic competition. Fifth, selectivity is readily examined, even for reactions that proceed near the collision rate.

Figure 1 (and Table I, supplementary material) summarizes the product yields for anions reacting with ethyl dimethyl phosphate under thermally equilibrated (298 K) conditions in a flowing afterglow.^{19,20} Only methoxide-*d*₃ clearly gives products from reaction at phosphorus and then only in 1.2% yield; fluoride may produce a trace amount ($\leq 0.6\%$) of reaction at phosphorus. Three mechanistic pathways (Scheme I) account for most of the products found: nucleophilic substitution (S_N2) at the methyl or methylene carbon yields (MeO)(EtO)PO₂⁻ or (MeO)₂PO₂⁻, respectively; elimination across the carbon-carbon bond (E2) also yields (MeO)₂PO₂⁻; elimination across a methyl- or methylene-oxygen bond (E_{CO2}) yields (MeO)(EtO)PO⁻ or (MeO)₂PO⁻.

The intrinsic competition between channels at a common methyl group is revealed by the unique products, (MeO)(EtO)PO₂⁻ and (MeO)(EtO)PO⁻; both S_N2-Me and E_{CO2}-Me are found for strongly basic (PA > 390 kcal mol⁻¹), localized anions. Amide and propyl amide yield more elimination (49.0%, 37.8%) than substitution (15.8%, 17.4%, respectively), whereas the weaker bases hydroxide and allyl anion yield more substitution (13.1%, 87.4%) at methyl than elimination (1.4%, 0.6%, respectively). Phenide, a strongly basic, localized carbanion also yields more S_N2-Me (62.4%) than E_{CO2}-Me (14.0%). For anions less basic than hydroxide, the only reaction occurring at methyl is substitution.

Therefore, while substitution competes poorly with elimination for strong, heteroatomic bases, substitution is preferred over elimination for carbanions.

E_{CO2}-Et mirrors E_{CO2}-Me; the highest yield is found for the strongest base (H₂N⁻, 10.3%), and lesser amounts are found for weaker localized or carbanionic bases (C₆H₅⁻, 3.6%; PrNH⁻, 5.1%; HO⁻, 0.6%; H₂C=CHCH₂⁻, 0%). Less of the E_{CO2}-Et pathway is observed than E_{CO2}-Me; this channel is not found for bases weaker than HO⁻. Of special note is the clear distinction that strongly basic, localized anions approaching an ethyl substrate bearing an excellent leaving group display reaction at the methylene carbon as well as the methyl carbon.

The (MeO)₂PO₂⁻ observed could be formed either by S_N2-Et or by E2-Et. The observation of (MeO)₂PO⁻ from E_{CO2}-Et for the strongly basic anions, however, reveals that elimination across a carbon-carbon bond is *not* the only reaction at the ethyl site and that some anions react at the methylene carbon in spite of the available E2-Et pathway. When the strongest localized bases, H₂N⁻ and PrNH⁻, react at ethyl, more (MeO)₂PO₂⁻ than (MeO)₂PO⁻ is formed, whereas their reactions at methyl yield more (MeO)(EtO)PO⁻ than (MeO)(EtO)PO₂⁻. Thus, (MeO)₂PO₂⁻ from reaction at ethyl must arise, at least in part, from elimination across the carbon-carbon bond, and therefore strongly basic anions react at *both* carbons of ethyl substrates bearing good leaving groups.

Three pairs of anions in Figure 1 allow us to compare reactivity between localized heteroatomic and delocalized carbanionic bases of identical basicity: hydroxide vs allyl, methoxide vs benzyl, and *tert*-butoxide (or fluoride) vs the conjugate base of acetonitrile. In each pair the localized anion yields far more (MeO)₂PO₂⁻ than (MeO)(EtO)PO₂⁻, while the opposite order is true for the delocalized carbanions. The striking difference in product distribution depends upon anion structure and remains constant over a wide range of basicities. This difference can only be explained by localized heteroatomic bases producing (MeO)₂PO₂⁻ by elimination at ethyl while delocalized carbon bases produce it by substitution. The preference of localized bases for E2 agrees with the conclusion reached by DePuy and co-workers;^{11,12} they did not examine delocalized anions. The preferential reaction of HS⁻ by substitution at methyl (64.3%) is consistent with the notion that sulfur anions are better nucleophiles than bases.^{11,12}

The observation of large changes in product yields as the anion reacting with ethyl dimethyl phosphate is varied emphasizes the great selectivity that is possible in gas-phase ion-molecule reactions. Strongly basic localized anions containing F, N, or O at the nucleophilic center react with appropriate substrates by preferential E2 reaction; in contrast, carbanions, particularly delocalized ones, prefer to react by displacement. Different types of anions of identical basicity display opposite selectivities, even where such reactions proceed at a high fraction of the encounter rate.^{17,21} The defined competition between reaction channels in the gas phase allows a more explicit definition of intrinsic reactivity-selectivity issues and should provide a stimulus for more exact computational modeling of the most fundamental reactions.

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Supplementary Material Available: Table of the product yields shown in Figure 1 and representative branching ratio plots for the reactions of HO^- and $\text{H}_2\text{C}=\text{CHCH}_2^-$ with ethyl dimethyl phosphate (5 pages). Ordering information is given on any current masthead page.

Fullerene Dications as Initiators of Polymerization with 1,3-Butadiene in the Gas Phase: Chemistry Directed by Electrostatics?

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One of the many emerging frontiers in fullerene chemistry is in the field of polymer chemistry. This is evidenced, for example, by the recent report of the synthesis of the first copolymer containing C_{60} , based on the reaction of the xylylene diradical with C_{60} dissolved in toluene.¹ We report here results of experiments which indicate that the dications of C_{60} and C_{70} may initiate the polymerization of the conventional polymerization monomer 1,3-butadiene in the gas phase. The results suggest a potential role for fullerene dications generally as initiators of polymerization. A novel feature of the proposed mechanism of this polymerization is the role which Coulombic repulsion between the two positive charges may play in driving the direction of polymerization.

Reactions of C_{60}^{2+} , C_{70}^{2+} , C_{60}^{2+} , and C_{70}^{2+} with 1,3-butadiene were monitored with a selected-ion flow tube (SIFT) apparatus.^{2,3} The fullerene cations were produced by electron bombardment (at 50 eV) of C_{60} and C_{70} vapor entrained in argon carrier gas. They were selected with a quadrupole mass filter, injected into helium buffer gas at 295 ± 2 K and 0.40 ± 0.01 Torr, allowed to thermalize by collisions with helium atoms, and finally exposed to 1,3-butadiene further downstream. The progress of the reactions was followed with a second quadrupole mass filter further downstream in the usual fashion.^{2,3} The 1,3-butadiene had a purity of $\geq 99.0\%$ (Matheson, C.P. grade). The fullerene powder was a mixture of C_{60} and C_{70} containing 2-12% C_{70} (Strem Chemicals Co.).

While C_{60}^{2+} and C_{70}^{2+} were found to be unreactive toward 1,3-butadiene, both C_{60}^{2+} and C_{70}^{2+} were observed to react rapidly with 1,3-butadiene with rate coefficients both equal to $(1.0 \pm 0.3) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, corresponding to nearly unit reaction efficiency (see Table I). Two primary product channels, charge-transfer and adduct formation, were identified, and these are elucidated in reaction 1 for C_{60}^{2+} . The observed variations



of individual ion signals are shown in Figure 1. The branching ratio for adduct formation (1a) to charge transfer (1b) was found to be 4:1 for C_{60}^{2+} and $>1:1$ for C_{70}^{2+} at the operating conditions of the experiments.

The best current value for the ionization energy of C_{60}^{+} , 11.39 ± 0.05 eV,^{4,5} makes charge transfer to 1,3-butadiene, which has an ionization energy of 9.07 eV,⁶ exothermic by 2.32 eV. This

Table I. Kinetic Data for Reactions of $\text{C}_{60}/\text{C}_{70}$ Cations with 1,3-Butadiene at 294 ± 2 K in Helium Buffer Gas at a Pressure of 0.40 ± 0.01 Torr

reactions	BR ^a	k_{obsd}^b	k_c^c
$\text{C}_{60}^{2+} + \text{C}_4\text{H}_6 \rightarrow$ none		<0.001	0.97
$\text{C}_{70}^{2+} + \text{C}_4\text{H}_6 \rightarrow$ none		<0.001	0.97
$\text{C}_{60}^{2+} + \text{C}_4\text{H}_6 \rightarrow \text{C}_{60}\text{C}_4\text{H}_6^{2+}$	0.8	1.0	1.94
$\rightarrow \text{C}_{60}^{+} + \text{C}_4\text{H}_6^{+}$	0.2		
$\text{C}_{70}^{2+} + \text{C}_4\text{H}_6 \rightarrow \text{C}_{70}\text{C}_4\text{H}_6^{2+}$	>0.5	1.0	1.93
$\rightarrow \text{C}_{70}^{+} + \text{C}_4\text{H}_6^{+}$	<0.5		

^a Branching ratio with an uncertainty of about $\pm 30\%$. ^b Apparent bimolecular rate coefficient in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with an uncertainty of about $\pm 30\%$. ^c Theoretical collision rate coefficient in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the ADO model of Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, Chapter 3, pp 83-118.

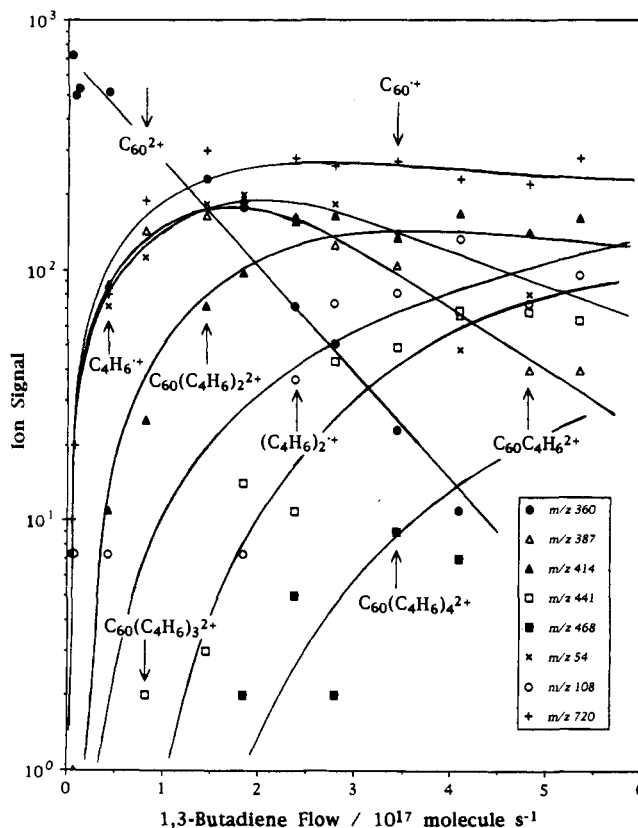
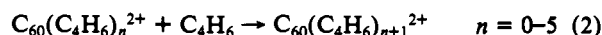


Figure 1. Observed variation in ion signals with the addition of 1,3-butadiene into the reaction region of the SIFT apparatus in which C_{60}^{2+} has been established as the dominant ion in helium buffer gas: $P = 0.40$ Torr, $\bar{v} = 6.9 \times 10^3 \text{ cm s}^{-1}$, nominal reaction length = 47 cm, and $T = 294$ K. C_{60}^{2+} is produced by electron impact at 50 eV on C_{60} vapor entrained in argon carrier gas.

exceeds the 2.06 eV which can be computed for the maximum height of the energy barrier to charge transfer which arises from Coulombic repulsion,⁷ so that the occurrence of some charge transfer is not surprising. Formation of the adduct presumably arises from collisional stabilization by helium atoms prior to dissociation to C_{60}^{+} and C_4H_6^{+} .

Figure 1 displays the observation of the occurrence of rapid sequential addition reactions which attach up to six molecules of butadiene to C_{60}^{2+} :



The butadiene radical cation produced in reaction 1b reacts with butadiene to form the dimer ion $(\text{C}_4\text{H}_6)_2^{+}$. The trimer of bu-

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