course of phosphoryl transfer from phenyl phosphate to *tert*-butyl alcohol in acetonitrile. This reaction was shown to proceed with almost complete racemization, in agreement with the results of this present study.

In the accompanying paper, the results of positional isotope exchange experiments complementary to the stereochemical study reported here are discussed. It is argued that the data would most support a preassociative stepwise mechanism for the phosphoryl transfer from ADP to alcohols in acetonitrile.

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Positional Isotope Exchange in Adenosine 5′-[β-$^{18}O_4$]Diphosphate and the Possible Role of Monomeric Metaphosphate

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Since monomeric metaphosphate (PO_3^-) was first postulated as an intermediate in the hydrolysis of monosubstituted phosphates 30 years ago,[1] much evidence has accumulated which is consistent with its intervention.[2] However, stereochemical analysis of the products formed when phenyl, 2,4-dinitrophenyl, and creatine [^{16}O,^{17}O,^{18}O]-(*R*)-phosphate were solvolysed in aqueous methanol under conditions where the intermediacy of monomeric metaphosphate had been invoked[2] showed that phosphoryl transfer proceeds with inversion.[3] Likewise, in the Conant–Swan fragmentation of 1,2-dibromo-2-phenylethyl[^{16}O,^{17}O,^{18}O]-(*R*)-phosphonate dianion, a reaction also considered to proceed by way of a metaphosphate intermediate,[4] phosphoryl transfer to an alcohol acceptor was also found to proceed with inversion.[5] The apparent conflict between the kinetic[2] and stereochemical evidence[3,5] can be reconciled, however, in terms of a preassociative mechanism.[6] In an attempt to provide a more sensitive probe of events occurring within the solvent cage during phosphoryl transfer reactions we have undertaken positional isotope exchange experiments with adenosine 5′-[β-$^{18}O_4$]diphosphate, prepared from adenosine 5′-phosphomorpholidate and mono(tri-*n*-butylammonium) [$^{18}O_4$]phosphate.[7]

The pK_a values of the diphosphate moiety of ADP are <1, 3.9, and 6.4.[8] [β-$^{18}O_4$]ADP was incubated in tris-HCl aqueous buffer (20 mM), in the presence of (a) $MgCl_2$ (0.5 M) and (b) EDTA (10 mM) at pH 5, 6, 7, 8, and 9 for 3 weeks at 20 °C, by which time approximately 20% [β-$^{18}O_4$]ADP had been hydrolyzed to [^{18}O]AMP and [$^{18}O_3$]P_i. The high-resolution ^{31}P NMR spectrum (101.232 MHz) of the recovered [$^{18}O_4$]ADP showed no evidence of positional ^{18}O exchange between the P_β-O-P_α bridge and the nonbridging sites at P_α in either experiment.

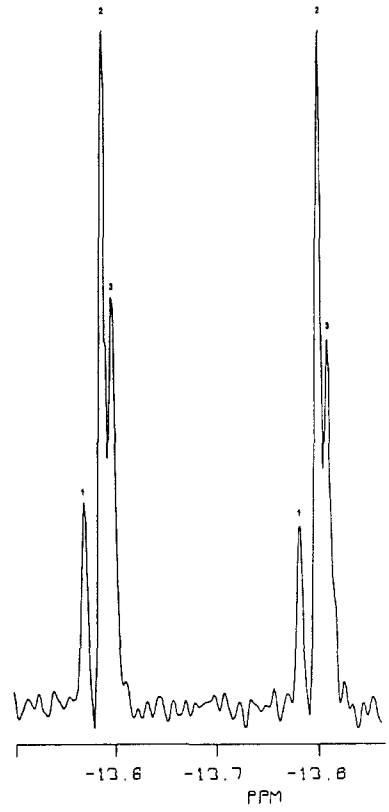

Figure 1. ^{31}P NMR spectrum (101.232 MHz) of P_α of the recovered isotopically labeled ADP after incubation of [β-$^{18}O_4$]ADP (87 atom % ^{18}O per site) in acetonitrile at 70 °C for 48 h. Assignments are 1, all species unlabeled at P_α; 2, all species with ^{18}O in P_α–O–P_β bridge; 3, all species with ^{18}O in nonbridging sites at P_α. The chemical shift reference is trimethyl phosphate.

Ramirez et al. have shown that ATP and ADP phosphorylated hindered alcohols (Pr-*i*-OH and Bu-*t*-OH) when incubated in acetonitrile at 70 °C and have proposed the intermediacy of monomeric metaphosphate.[9] [β-$^{18}O_4$]ADP tris(tetra-*n*-butylammonium) salt was incubated alone in dry acetonitrile at 70 °C in a drybox and after 2 days the four components present were separated by HPLC and identified as AMP, ADP, adenosine 2′,5′-biphosphate (pAp), and adenosine 2′-phospho-5′-diphosphate (ppAp). High-resolution ^{31}P NMR spectroscopy showed the AMP to be singly ^{18}O labeled and the pAp and ppAp to be triply ^{18}O labeled at the 2′-phosphate group. The high-resolution ^{31}P NMR spectrum of the recovered ADP (and the ppAp) showed that extensive ^{18}O exchange from the P_β-O-P_α bridge to the nonbridging site at P_α had occurred (Figure 1).

The possibility that the positional isotope exchange had occurred by $P_\beta{}^{18}O_3$ transfer from [β-$^{18}O_4$]ADP to [^{18}O]AMP formed in situ was excluded by a control experiment in which [$^{18}O_2$]AMP was incubated with unlabeled ADP (as their tetra-*n*-butylammonium salts) in acetonitrile at 70 °C for 12 h by which time about 60% of the ADP had been converted to other products. The recovered ADP remained completely unlabeled demonstrating that ADP does not transfer $P_\beta O_3$ to the phosphate moiety of AMP, presumably owing to electrostatic repulsion.

Failure to observe positional isotope exchange in [β-$^{18}O_4$]ADP (or its Mg^{2+} complex) after incubation as its di- and trianion in aqueous solution is consistent with a preassociative concerted

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mechanism. The preassociative stepwise mechanism only remains tenable if one assumes that the lifetime of the putative intermediate [H_2O·PO_3^-·AMP] complex is so short that it always collapses back to starting material faster than rotation about the O_3P–O bond of AMP can occur within the complex.

Positional isotope exchange of [β-$^{18}O_4$]ADP in acetonitrile is consistent with the preassociative stepwise mechanism, the [CH_3CN·PO_3^-·AMP] complex collapsing back to the CH_3CN·ADP encounter complex faster than acetonitrile can diffuse from it. The possibility that the product [CH_3CN^+–PO_3^{2-}·AMP] complex (which would be the same for both the concerted and stepwise mechanism) is responsible for allowing positional isotope exchange to occur thereby introducing mechanistic ambiguity is, however, difficult to rigorously exclude although the control experiment suggests that the lifetime of the [CH_3CN^+–PO_3^{2-}·AMP] is too short for phosphoryl transfer to the phosphate group of AMP to occur.

The above observations suggest that when water or an alcohol preassociates with ADP (and presumably other monosubstituted phosphates) a concerted transfer of the phosphoryl group is likely leading to inversion of configuration, although the possibility of a stepwise mechanism occurring especially if the leaving group has an exceptionally low pK_a cannot be excluded. If, however, preassociation occurs with a weak nucleophile such as acetonitrile, ethers, etc. which cannot form a stable phosphorylated product, the extent to which it can compete with the ultimate acceptor will determine the degree of racemization observed in stereochemical experiments. As reported in the preceding paper, incubation of adenosine 5'-[β-^{16}O,^{17}O,^{18}O]-(*S*)-diphosphate as its trianion in acetonitrile with 2-O-benzyl-(*S*)-propane-1,2-diol as the ultimate acceptor leads to almost complete racemization with a small degree of retention.[10] This observation suggests that the ultimate product is formed by way of CH_3CN^+–[^{16}O,^{17}O,^{18}O]PO_3^{2-} and that the [^{16}O,^{17}O,^{18}O]PO_3^- moiety is usually transferred to other acetonitrile molecules before it is captured by the ultimate acceptor, but it is also possible that the (CH_3CN·[^{16}O,^{17}O,^{18}O]PO_3^-·AMP) complex on the stepwise pathway has a lifetime long enough for the [^{16}O,^{17}O,^{18}O]PO_3^- moiety to tumble and contribute to racemization.

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Resonance in C_{60}, Buckminsterfullerene†

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Recently Kroto et al.[1] have found that laser vaporization of graphite in a high-pressure supersonic nozzle produces a remarkably stable C_{60} molecule in high yield. It was argued that this new species takes the form of a truncated icosahedron with C atoms at each of the vertices and σ-bonds along each edge, and in recognition of Buckminster Fuller's studies of such (geodesic-dome-like) structures the name buckminsterfullerene was suggested. The remaining π-bonds delocalized through resonance were presumed to account for the indicated high stability. Here we report energy calculations for this soccerball-like structure via quantitative resonance theories and make comparisons to simple Hückel MO results.

The proposed structure has icosahedral symmetry including inversion, $I_h = I \times C_i$ so that the Hückel molecular orbitals are labeled by irreducible representations of I and C_i. The orbital energies of these various symmetries appear in Table I. The A, F_1, F_2, G, and H representations of I yield 1-, 3-, 3-, 4-, and 5-fold degeneracies of the associated levels (so that overall there are 30 antibonding and 30 bonding π-MO's). The + and − labels identify the C_i symmetry.

Table I. Orbital Energies and Symmetries[a]

	+	−
A	−3.000	
F_1	+0.382	−2.757, +0.139
F_2	+2.618	−1.820, +1.438
G	−1.000, +2.000	−1.562, +2.562
H	−2.303, −1.000, +1.303	−0.618, +1.618

[a] In units of $|\beta|$, with $\alpha = 0$.

Table II. Various Resonance Energies for Several Species

	Hückel MO, β	Kekulé count,[a] J	conjugated circuit,[b] eV
C_{60}			
uncorrected	0.553	−0.178	−0.120
corrected	0.509	−0.150	−0.101
benzene	0.333	−0.131	−0.140
pentacene	0.388	−0.092	−0.084
coronene	0.440	−0.141	−0.146
graphite	0.575	−0.183	−0.168

[a] Calculated from eq 4, ref 3b, as corrected: *Chem. Phys. Lett.* **1985**, *118*, 1101. [b] Calculated from eq 1, truncated after 10 cycles, R_1 = −0.841 eV, R_2 = −0.336 eV.

The number of Kekulé structures for this molecular species provides another indication of its stability. We have carried out this enumeration via a recently implemented transfer matrix technique[2] and find that there are (exactly) K = 12500 Kekulé structures. The logarithm of such a count has been argued[3] to be proportional to the resonance energy. Pauling bond orders[4] may be obtained by taking the ratio of the number of Kekulé structures with a double bond between a particular pair of atoms to K. This leads to bond orders of 7/25 for edges separating pentagonal and hexagonal faces and 11/25 for edges separating two hexagonal faces.

We also apply the Herndon–Simpson resonance theory[5] (with an underlying valence-bond rationale) or the conjugated-circuit method[6] (with an empiric rationale related to Clar's[7] ideas). In these methods the resonance energy is given as a ratio H/K, with

$$H = \sum_{n\geq 1}\{\#^{2n+2}R_n + \#^{2n}Q_n\} \qquad (1)$$

where the R_n and Q_n are (exchange matrix element) parameters and $\#^{2m}$ is the sum over the number of conjugated $2m$ circuits in the various Kekulé structures. (Here a conjugated $2m$ circuit in a Kekulé structure is a length $2m$ cycle with alternating single and double bonds.) Again utilizing the transfer matrix approach[2] we obtain $\#^6$ = 83 160, $\#^8$ = 0, $\#^{10}$ = 59 760, $\#^{12}$ = 50 880, and $\#^{14}$ = 44 760.

Computation of explicit resonance energy estimates requires consideration of the effects of the molecule's nonplanarity upon the model parameters. The angle between nearest-neighbor sites (and hence the twist angle between π-orbitals oriented normal to the "sphere" surface) as measured from the center of the cage is $\cong$23° if all the bond lengths are similar. Thence the overlap and one-electron resonance integrals should be reduced from their ordinary planar values by a factor $\cong$ cos 23° $\cong$ 0.92. Likewise two-electron exchange integrals should be reduced by a factor $\cong$

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