dational experiments also imply that the parent ion derives from the 
Fe*^*(T_d^3d^4s) ground state rather than the Fe*^*(F^3d^7) first 
extcited state. Specifically, recent measurements find that bond 
energies for Co*–alkane complexes are consistently stronger than 
the analogous Fe*–alkane species, contrary to the similar alkane 
bond strengths expected for Co*^*(3d^9) and Fe*^*(3d^7).

Since reactions 2a and 1b (which are exothermic by 19 and 
11 ± 5 kcal/mol, respectively) exhibit no activation barriers, 
reactions 2a and 2b must have lower thermodynamic thresholds 
than process 2c, as is evident from Figure 1. Analyses of these 
two products find a threshold of 0.47 ± 0.12 eV (11 ± 3 kcal/mol) 
for both processes, even though reactions 2a and 2b have different 
activation enthalpies, ~0 and 8 kcal/mol, respectively, given 
D*(Fe*–C_3H_8) = 19 kcal/mol. Clearly, the observed threshold for 
reaction 2a is not the thermodynamic threshold, but rather 
the activation barrier associated with the rate-limiting step in the 
bimolecular process. It seems likely that this is also true for 
reaction 2b. In analogy with recent work on the Co*+propane 
system (based on completely different experimental techniques),
we propose that this barrier corresponds to the activation of a C–H 
bond of propane by Fe*.

Further insight into the PES can be obtained from the kinetic 
energy dependence of reactions 2a and 2b. For the bimolecular 
system, reaction 1a is favored by a factor of 3 at all kinetic energies 
for both the 6D and 4F electronic states of Fe*, consistent with 
the Fe+(6D,3d^64s) ground state rather than the Fe+(4F,3d^7) first 
electronic state. Specifically, recent measurements find that bond 
strengths expected for Co+(3d^8) and Fe+(3d^7).

The combination of all these results leads to the PES shown in Figure 2. This diagram clearly does not indicate all of the 
complications of the system, in particular the surfaces of differing 
spins that arise from the two lowest energy states of Fe*. Further 
work to probe the PES of this interesting reaction system is 
underway. Such studies will include examination of the reverse 
of reactions 2a and 2b and, if possible, TCA of other purported 
intermediates on the PES.

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Primary and Secondary Oxygen-18 Isotope Effects in 
the Alkaline and Enzyme-Catalyzed Hydrolysis of 
Phosphotriesters

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Phosphotriester hydrolysis occurs by an associative mechanism 
with nucleophilic attack of hydroxide. This associative process 
can occur via two limiting mechanistic alternatives: the formation

(10) Thermochemistry for organic species is taken from the following: 
Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, 
90, 445; Peiley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochanical Data of 

(11) Our preliminary work on the CID of FeC_3H_6^+ and FeC_2H_4^+ yields 
bond strengths in agreement with those of ref 12 (Schultz, R. H.; Armentrout, 
P. B., work in progress).

(12) van Koppem, P. A. M.; Bowers, M. T.; Beauchamp, J. L.; Dearden, 
D. V. In Bonding Energries in Organometallics Compounds; Marks, T. J., 

(13) van Koppem, P. A. M.; Brodbelt-Lustig, J.; Bowers, M. T.; Dearden, 

(11) Benkovic, S. J.; Schray, K. J. Enzymes (3rd Ed.) 1973, 8, 201. Khan, 
of a pentavalent phosphorane intermediate (eq 1) or a direct \( S_n 2 \)-like reaction (eq 2). With cyclic phosphotriesters where pseudorotation is necessary for the leaving group to leave axially, a phosphorane intermediate is predicted. However, for the chemical hydrolysis of acyclic phosphotriesters, neither mechanistic changes to both the phosphoryl oxygen and the phenolic leaving group are limited by bond breaking. In an effort to further define the enzymatic mechanism, as well as to provide evidence for the mechanistic alkaline hydrolysis of phosphotriesters, \( ^{18} \)O isotope effects for the phenolic and phosphoryl oxygen atoms were measured. The magnitude of the \( ^{18} \)O isotope effects at these two positions should provide direct information on the changes that have occurred in these phosphorus-oxygen bonds in the transition state. The \( ^{18} \)O isotope effects were measured by the remote label method, where the \( ^{15} \)N,\( ^{18} \)O compound and the \( ^{14} \)N (\( ^{15} \)N depleted) compound were combined to give a resulting mixture very near the natural abundance ratio for nitrogen. The \( ^{18} \)O isotope effect was determined by separating the phenol from the residual substrate after about 50% hydrolysis (hydrolysis performed with 0.1 N KOH or the phosphotriesterase), and then each was subsequently converted separately to diatomic nitrogen by Kjeldahl digestion, alkaline steam distillation, and oxidation. In the case of paraoxon, the nitro group was first reduced in the presence of sodium thiosulfate. The mass ratio of the isolated nitrogen was measured by using an isotope ratio mass spectrometer. The oxygen isotope effects are presented in Table I.

The \( ^{18} \)O isotope effects of 1.006 and 1.0063 for the alkaline hydrolysis of paraoxon provide strong evidence that significant bond-order changes have occurred to both the phosphoryl and phenolic oxygen in the transition state. The isotope effect for the phenolic oxygen is very similar to the value of 1.007 obtained for the hydrolysis of 2,4-dinitrophenyl dibenzyl phosphate measured by a direct spectrophotometric method. A primary \( ^{18} \)O isotope effect of this size would not be expected for the formation of a discrete phosphorane intermediate since the rate-determining step is most likely the addition of hydroxide to the transition state.

Table I. Primary and Secondary Isotope Effects for the Alkaline and Enzyme-Catalyzed Hydrolysis of Paraaxon (I) and \( O,O \)-Diethyl \( O,4 \)-Carbamoylphenyl Phosphate (II)

<table>
<thead>
<tr>
<th>compd</th>
<th>isotope effect</th>
<th>( \Delta E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I )</td>
<td>1st alkaline</td>
<td>1.0058</td>
</tr>
<tr>
<td>( I )</td>
<td>1st enzymatic</td>
<td>1.0020</td>
</tr>
<tr>
<td>( I )</td>
<td>2nd alkaline</td>
<td>1.0056</td>
</tr>
<tr>
<td>( I )</td>
<td>2nd enzymatic</td>
<td>1.0024</td>
</tr>
<tr>
<td>( I )</td>
<td>1st alkaline</td>
<td>1.023</td>
</tr>
<tr>
<td>( I )</td>
<td>1st enzymatic</td>
<td>1.036</td>
</tr>
<tr>
<td>( I )</td>
<td>2nd alkaline</td>
<td>1.020</td>
</tr>
<tr>
<td>( I )</td>
<td>2nd enzymatic</td>
<td>1.0144</td>
</tr>
</tbody>
</table>

The following equation was utilized to calculate the \( ^{18} \)O isotope effect (\( \Delta E \)): \( \Delta E = \left( \frac{W}{W_0} \right)^2 - 1 \), where \( W \) is the observed isotope effect, \( \frac{W}{W_0} \) is the \( ^{18} \)O isotope effect at the remote labeled position determined with natural abundance phosphotriesterase (1.007 \( \pm \) 0.0001) for the chemical hydrolysis of I, 1.000 for the enzymatic hydrolysis of I and II, and 1.000 for the chemical hydrolysis of II), \( B \) is the fraction of \( ^{15} \)N,\( ^{18} \)O-containing phosphotriesterase in the final mixture or pseudo natural abundance phosphotriesterase (0.003851 for I \( 1^o \), 0.003602 for II \( 1^o \), and 0.003629 for II \( 2^e \)), \( Y \) is the fraction of \( ^{15} \)O in the \( ^{15} \)N,\( ^{18} \)O phosphate triester (0.88 for I \( 1^o \), 0.80 for I \( 2^e \), 0.89 for II \( 1^o \), and 0.82 for II \( 2^e \)). \( X \) is the fraction of \( ^{15} \)N in the \( ^{15} \)N,\( ^{18} \)O phosphotriesterase (0.99), and Z is the fraction of \( ^{15} \)N in the \( ^{15} \)N,\( ^{18} \)O phosphotriesterase (0.0001). The observed isotope effects were determined from comparative isotopic analysis between either the residual phosphotriesterase, the phenol product, or both after approximately 50% reaction, and the initial phosphotriesterase. Only one determination of this number was made.

The isotope effect for the phenolic oxygen in the transition state. The isotope effect for the phenolic oxygen is very similar to the value of 1.007 obtained for the hydrolysis of 2,4-dinitrophenyl dibenzyl phosphate measured by a direct spectrophotometric method. A primary \( ^{18} \)O isotope effect of this size would not be expected for the formation of a discrete phosphorane intermediate since the rate-determining step is most likely the addition of hydroxide to the transition state.

(9) The formation of a phosphorane intermediate could, however, result in the shortening (or loosening) of the phosphorus phenolic bond as the leaving group adopts an axial position. This change in geometry could cause a secondary \( ^{18} \)O isotope effect from the phenolic oxygen due to changes in the stiffness of this bond.
(13) Sims, L. B.; Burton, G.; Lewis, D. E. BEBIVOB-IV Program, No. 337, Quantum Chemistry Exchange Programs; Department of Chemistry, Indiana University: Bloomington, IN.

These two volumes are paginated continuously, and the index, covering both, is only in Part 2, although the volumes can apparently be bought separately. Their content consists of one group of chapters devoted to subjects not treated before in this series and another group of “integrative” chapters, in which a “unified and comparative treatment of several double-bonded functional groups together” is presented. The nine chapters in the latter category make up most of Part 1. They cover various topics such as homopolar bond structure, mass spectrometry, NMR, photoelectron spectroscopy, directing and activating effects, biochemical perspectives on double bonds, intramolecular 1,3-dipolar cycloadditions, the eve reaction, and radiation chemistry. The former category includes asymmetric induction in addition to C=O and C≡N double bonds, electrophilic additions to C≡C double bonds, mechanisms of base-catalyzed 1,2-eliminations, carbonylation of main-group organometallic compounds, rearrangements involving allenes, 1,1-diarylkalkenes, fulvenes, the thio-carbonyl group, and cycloadditions of enones.

The literature coverage is “up to about the end of 1987 and in some cases even to the middle of 1988”, and the bibliographies are extensive. As is characteristic of the series, there are good tables of data and an abundance of carefully drawn structure formulas.

The writing is essentially critical, insofar as the subject matter allows, and the contributors have successfully avoided presenting a mere recapitulation of facts. The valuable content is made accessible by a 22-page index of professional quality, augmented by a true author index of impressive magnitude.

This is an important work of basic reference, which should be acquired by all libraries serving organic chemists.


This book is an English translation of a German textbook by W. Creuger and A. Creuger. Professor T. D. Brock again did a commendable job in the translation. When one goes over the English version, there is no hint or evidence whatsoever that this is a translated version. When this reviewer took Industrial Microbiology under Professor A. L. Demain at MIT, he saved most of the lecture notes and articles given by Dr. Demain. This book literally replaces all these old notes and more. The book is divided into two parts. Chapters 1–6 discuss the traditional practices by the industrial microbiologists and bioengineers. The materials are condensed but they are usually a good start for students and scientists with minimal exposure to this area. The amount of information on fermentation (Chapter 5) and product recovery (Chapter 6) may be useful as background materials for many biologists and chemists. Bioengineers on the other hand, may find them too little and too sterile of any practical use. Again, it is a good start for non-engineering scientists and students unfamiliar with these subject matters. There are sufficient references at the back of each chapter for them to explore further any interesting topics.

Chapters 7–20 are divided based on product classifications. It is striking that there is no separate chapter on recent cell culture derived or recombinant DNA technology derived bioproducts such as TPA, HGH, r-insulin, etc. Only traditional fermentation derived products are emphasized with minimal discussion on the impact of recombinant technology on those products. Waste treatment is treated in Chapter 17 with little discussion on toxic waste remediation.

Overall, the book is well-written and well-organized. The new edition did include some information of recombinant DNA techniques on strain selection and new product development. But, these additions did not seem to distinguish the new edition from the first one. It is well-suited as a reference book for undergraduate level exposure to the field of industrial microbiology. Given the broad areas that the authors try to cover, some sacrifice on substance is inevitable. It is indeed a good book for many lay researchers to start and want to join in with the biotechnology revolution.


This volume of the Coal Science and Technology series provides a strong overview of many of the different spectroscopic techniques that have been applied to the analysis of coal liquids. The broad range of techniques discussed in this volume include gas chromatography (K. D. Burtie), pyrolysis and hydrolysis (W. Steedman), mass spectrometry (B. D. Butts and J. E. Batts), infrared spectroscopy (P. M. Fredricks), ultraviolet and luminescence spectroscopy (J. R. Kershaw), nuclear magnetic resonance (M. I. Attalla, A. M. Vassallo, and M. A. Wilson), and continuous wave and pulsed electron spin resonance spectroscopy (S. Schlick and L. Kevan). Each of the contributors provides an overview of the technique as well as an in-depth discussion of its use in the analysis and corresponds to a bond order of about 1.38. This is anticipated since 4-hydroxybenzamide is a somewhat poorer leaving group compared to p-nitrophenol.

The primary and secondary ¹⁸O isotope effects measured for the enzymatic hydrolysis of paraxonal (I) are 1.0020 and 1.0021, respectively. These isotope effects are much smaller than those observed for nonenzymatic hydrolysis and are consistent with previous data which indicate that the chemical step is not totally rate limiting. However, with the nonsticky substrate II, the primary and secondary ¹⁸O isotope effects are 1.036 and 1.018, respectively. These values are similar to those for alkaline hydrolysis and therefore support the chemical step as totally rate limiting in the enzymatic hydrolysis of this substrate. At present, a complete interpretation of the measured isotope effects for the enzymatic mechanism is limited since the potential participation of active-site residues and a required zinc atom is unknown. Experiments are underway that will better define the role of the zinc atom in catalysis.

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*Unsigned book reviews are by the Book Review Editor.