Γ_C and Γ_D are slightly below the uncertainty limits we assigned. On the other hand, it is also possible that there is some small amount of geminate rebinding with a time constant near 2 to 5 ns that has escaped detection by either of our instruments.

Gibson et al.[37] report that for WhMbCO, $Q = 1.00 \pm 0.07$. Earlier work suggested 0.95[18] or 1.0.[40] These results are consistent with the observations of Henry, et al.,[26] who found 4% recombination of geminate pairs of CO to myoglobin with a time constant of 180 ns after photolysis with 10-ns, 532-nm pulses. Our results agree and we conclude that the product of all factors $\Gamma_B\Gamma_C\Gamma_D$ is indeed very close to unity.

In the case of whale myoglobin, approximately 85% of the initially photolyzed NO rebinds on the picosecond time scale. The value of Q cited by Antonini et all.[18] is less than 0.001, while Gibson et al.[37] specify less than 0.01. Either number means that about 15% of ligand rebinding takes place in the nanosecond range. This suggests that the recombination of NO to whale myoglobin from geminate pairs also has a nanosecond as well as a picosecond component. Since Γ_C is measurably smaller in ElMbNO, we would predict that Q for elephant would be even lower than in whale. We know of no measurement. Unfortunately, Q for WhMbNO is already so small as to be difficult to measure precisely; measuring Q for ElMbNO should be even more challenging.

Ours is not the first study to invoke a multistate mechanism to describe the rebinding of ligands to hemoproteins,[7,41] in specific, to sperm whale myoglobin.[6,26,37] Gibson et al.[37] invoke a four-state model, and they attempted an intricate deconvolution procedure to extract fast processes from their data, obtained using 30-ns laser pulses. In the end, however, all their reported rate constants remain slower than 10^8 s^{-1}, except for the unique instance of k_{BA} for WhMbNO (their k_2), for which they infer a value of 1.6×10^{10} s^{-1}, quite close to the slower of the two processes we measure directly in this case. We find processes faster than 10^{10} s^{-1} in all complexes, except WhMbCO.

Although the four-state model is more specific and complex than has been used in the past to treat aqueous solutions of MbL at ambient temperatures, it may still not do full justice to the complexity of protein–ligand interactions. Austin et al.[6] find evidence for multiple intermediates in the dissociation of MbL in glasses at low temperatures. We have some doubt that those intermediates will survive as identifiable, distinguishable species in ambient solution; but the matter is far from settled. It may eventually become possible to correlate features of the picosecond kinetics with aspects of the low-temperature kinetics. In the meantime, our results are accurately accommodated by the four-state model.

Conclusion

We present experimental results which clearly show that the geminate recombination of oxygen and several isocyanides with whale myoglobin is at least a two-intermediate process and can be modeled with a four-state model. The two intermediate states are strikingly different forms of the geminate pair: the contact pair returns with rate constant $k_{BA} > 10^{10}$ s^{-1}, while the separated pair reforms the contact pair with rate constant $k_{CB} \simeq 10^7$–10^8 s^{-1}. Other ligands, specifically CO and NO, do not reveal both processes at current experimental resolution but are easily understood as limiting cases. CO exhibits so little recombination from the geminate pair that we cannot detect it on either time scale; NO exhibits so much fast recombination that there is too little left to detect in the slow process. A variety of ligands, including imidazoles, would be expected to show picosecond recombination reactions with other transition-metal systems. Further experiments are in progress along these lines.

We have also found that steric interactions occur very early in the ligand-binding process. Differentiation between ligands occurs as the ligand enters the protein and not at the iron binding site as has been widely thought. The difference in the overall association rates is determined by ligand size and the rate of ligand motion through the protein into the pocket. After the ligand has diffused to the binding site and orients itself in the necessary configuration with respect to the heme plane, bond formation is very rapid. Except in the case of CO, the rate of bond making is approximately the same for the diatomics as for the bulkier isocyanides. The rate of formation of the separated pair from the contact pair is nearly the same in all cases, again regardless of ligand size. In light of the results concerning the rebinding of isocyanides, it is necessary to further investigate the combination properties of Lewis bases with metal systems.

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(40) Brunori, M.; Giacometti G. M.; Antonini, E.; Wyman, J. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 3141–3144.

(41) Friedman, J. M. *Science* **1985**, *228*, 1273–1280.

(42) **Note Added in Proof.** A recent report is the following: Houde, D.; Petrich, J. W.; Rojas, O. L.; Poyart, C.; Antonetti, A.; Martin, J. L. *Ultrafast Phenomena V*; Springer-Verlag: Berlin, 1986; pp 419–422.

Gas-Phase Reactions of $LaFe^+$ with Alkanes

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Abstract: The formation and reactions of $LaFe^+$ with saturated hydrocarbons are reported. Laser-generated La^+ reacts with iron pentacarbonyl to yield predominantly $LaFe(CO)_3^+$, which upon collisional activation yields $LaFe^+$. The reactions of $LaFe^+$ with alkanes are quite different from that of either La^+ or Fe^+. Dehydrogenation is common for the reactions of $LaFe^+$ with alkanes. Dehydrogenation and methane elimination are observed for the reaction of neopentane with $LaFe^+$. Carbon–carbon cleavage and dehydrogenation occur in the reactions of $LaFe^+$ with C_3 and C_4 cyclic alkanes, while dehydrogenation is observed exclusively for cyclopentane, cyclohexane, and methylcyclohexane. The reactivity of $LaFe^+$ is particularly interesting in that several other heterodinuclear ions have been observed to be unreactive with alkanes, although their constituent monoatomic ions are reactive. $D°(La^+–Fe)$ was determined to be 48 ± 5 kcal/mol by photodissociation.

The physical and chemical properties of small metal clusters and their ionic counterparts have been attracting increasing interest over the past decade.[1,2] Both experimental and theoretical research on small metal clusters have been fueled because of their

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important role in astronomy, the photographic process, homogeneous nucleation, surface science, and heterogeneous catalysis.[3]

Gas-phase techniques are ideally suited for the study of metal clusters and new methods are frequently being reported. Knudsen cell mass spectrometry has yielded bond energies for most homonuclear transition metal dimers.[4] A variety of metal cluster ions have been produced by electron impact[5,6] and multiphoton ionization of metal carbonyls.[7] Supersonic beams have proven especially useful for generating relatively large metal clusters of varying sizes.[8-10] The marriage of this supersonic beam technology with Fourier transform mass spectrometry promises to provide a particularly powerful method for studying the relationship between the size and reactivity of cluster ions.[11] Recently, sputtering techniques using high-energy atom beams have proven valuable for producing and studying metal cluster ions of varying sizes.[12-14] In addition, rare-gas matrix isolation methods have also been used to study dinuclear molecules.[15-18]

A convenient method of synthesizing small metal cluster ions in situ by reacting gas-phase metal ions with volatile metal carbonyl complexes has been developed in our laboratory.[19] Photodissociation studies on these heteronuclear cluster ions have provided useful information concerning their absorption characteristics and bond energies.[20] Detailed studies on the reactivity of several heterodinuclear ions with hydrocarbons have thus far been reported. One interesting trend which has been observed is that, although monoatomic gas-phase transition metal ions are generally very reactive toward saturated hydrocarbons,[21,22] dinuclear metal ions such as Co_2^+,[6] $CoFe^+$,[23] VFe^+,[24] and $CuFe^+$ [25] are totally unreactive. The species Co_2CO^+ [6] and the trimer ion, $FeCo_2^+$,[26] however, are once again reactive. This change of reactivity with cluster size and attached ligands suggests that probably some electronic factors arising from metal–metal interactions are important in determining the cluster ion reactivity. However, understanding the reactivities of even these small transition metal cluster ions awaits a detailed theoretical treatment of the metal–metal bonding in these species. Furthermore, it is evident that the study of additional cluster systems is necessary before clear patterns linking cluster size and makeup with reactivity begin to emerge. In this study, we expand a preliminary report involving $LaFe^+$.[27] Contrary to the above-mentioned dinuclear ions, $LaFe^+$ is found to be reactive with all linear, branched, and cyclic alkanes studied except methane.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer, previously described in detail,[28] which is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell utilizes two stainless steel screens of 80% transmittance as the transmitter plates, permitting irradiation of the interior with various light sources. La^+ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 532 nm) onto a thin high-purity lanthanum foil which is supported on the opposite transmitter plate. Details of the laser ionization experiment are described elsewhere.[29]

All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. Sample pressures were measured with an uncalibrated Bayard-Alpert ionization gauge and were typically 4×10^{-7} torr. For collision-induced dissociation (CID) experiments, Ar was added yielding a total pressure of approximately 4×10^{-6} torr.

The product ion distributions are reproducible to ±10% absolute. Secondary reactions were observed by using swept double-resonance ejection procedures to isolate the ions of interest.[30] Isolated ions were then allowed to react and the products observed.

The major primary product ion structures were investigated by collision-induced dissociation. Details of the CID experiments have been discussed previously.[31] The translational energy of the ions is given in the laboratory frame and can be varied typically between 0 and 100 eV. The spread in kinetic energy is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV. Because of the multiple collision conditions required to observe CID using FTMS,[31] rearrangement can occur prior to dissociation, obscuring the diagnostic information. Low signal-to-noise often prevented further structural studies on CID product ions. Thus, many of the structures are assigned as "reasonable" as opposed to proven. Neutral products from gas-phase ion–molecule reactions are generally inferred from the reaction. In the following discussion, when more than one alternative is possible, the neutral species are put in parentheses to designate that their exact identity is not known.

$LaFe^+$ was generated and studied by the following procedure originally reported for $CoFe^+$.[19] Laser-desorbed lanthanum ion, La^+, was permitted to react with $Fe(CO)_5$, displacing two carbonyls as indicated in reaction 1. The product ion in reaction 1 was then isolated by swept double

$$La^+ + Fe(CO)_5 \rightarrow LaFe(CO)_3^+ + 2CO \qquad (1)$$

resonance ejection pulses and accelerated to 68-eV kinetic energy. Collision with the Ar target gas stripped away the remaining carbonyls consecutively, reaction 2, and the bare cluster ion was then isolated and

$$LaFe(CO)_3^+ \xrightarrow{-CO} LaFe(CO)_2^+ \xrightarrow{-CO} LaFeCO^+ \xrightarrow{-CO} LaFe^+ \qquad (2)$$

allowed to react with a variety of different samples. The $LaFe^+$ ions generated by reaction 2 undoubtedly are formed with a distribution of internal energies. The CID collision gas was maintained at a high pressure relative to the hydrocarbon reagent gas pressure, therefore, in order to allow excess energy to be dissipated by thermalizing collisions with argon prior to reaction. A rough estimate from the experimental conditions gives an average of about 25 collisions with Ar before the dimer ion reaction is monitored. A linear pseudo-first-order decay plot obtained for $LaFe^+$ reacting with propane for over 80% of the $LaFe^+$ population indicates that the majority of the ions are thermalized. The presence of a small population of nonthermal dimer ions, however, cannot be completely ruled out.

Further reactions of the bare cluster ion with $Fe(CO)_5$ can severely interfere with the reactions of $LaFe^+$ with alkanes. This problem was minimized by using a General Valve Corp. Series 9 pulsed solenoid valve to add $Fe(CO)_5$ to a maximum of 10^{-5} torr after which the remaining gas was pumped away in about 250 ms by a 5-in. diffusion pump.[32]

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(1) (a) Kappes, M. M.; Schumacher, E. *Surf. Sci.* **1985**, *159*, 1. (b) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049.

(2) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *Surf. Sci.* **1985**, *156*, 8.

(3) (a) Montano, P. A.; Shenoy, G. K.; Alp, E. E.; Schulze, W.; Urban, J. *Phys. Rev. Lett.* **1986**, *56*, 2076. (b) Ozin, G. A.; McIntosh, D. F. *J. Phys. Chem.* **1986**, *90*, 5756.

(4) Gingerich, K. A.; Shim, I.; Gupta, S. K.; Kingcade, J. E., Jr. *Surf. Sci.* **1985**, *156*, 495.

(5) Ervin, K.; Loh, S. K.; Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1983**, *87*, 3593.

(6) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(7) Leopold, D. G.; Vaida, V. J. *J. Am. Chem. Soc.* **1983**, *105*, 6809.

(8) Smalley, R. E. *Laser Chem.* **1983**, *2*, 167.

(9) Kaldor, A.; Rohlfing, E.; Cox, D. M. *Laser Chem.* **1983**, *2*, 185.

(10) Bondybey, V. E. *J. Chem. Phys.* **1982**, *77*, 3771.

(11) Alford, J. M.; Williams, P. E.; Trevor, D. J.; Smalley, R. E. *Int. J. Mass Spectrom. Ion Phys.* **1986**, *72*, 33.

(12) Hanley, L.; Anderson, S. L. *Chem. Phys. Lett.* **1985**, *122*, 410.

(13) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202.

(14) Magnera, T. F.; David, D. F.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 936.

(15) Baetzold, R. C. *J. Chem. Phys.* **1971**, *55*, 4355, 4363.

(16) Anderson, A. B. *J. Chem. Phys.* **1975**, *62*, 1185.

(17) Schulze, W.; Becker, H. U.; Abe, H. *Chem. Phys.* **1978**, *35*, 177.

(18) Moskovits, M.; Hulse, J. E. *J. Chem. Phys.* **1977**, *66*, 3988; **1977**, *67*, 4271.

(19) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623.

(20) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 3537.

(21) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

(22) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120.

(23) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 1581.

(24) Hettich, R. L.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 6222.

(25) Tews, E. C.; Freiser, B. S. J. *Am. Chem. Soc.* **1987**, *109*, 4433.

(26) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 5351.

(27) Huang, Y.; Buckner, S. W.; Freiser, B. S. In *Physics and Chemistry of Small Clusters*; *NATO Advanced Science Institutes Series, Series B: Physics*; Jena, P., Rao, B. K., Khanna, S. N., Eds.; Plenum Press: New York, 1987; Vol. 158.

(28) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(29) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

(30) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

(31) Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

$D°(La^+-Fe)$ was determined by photodissociation. The details of the photodissociation experiments are described elsewhere.[33] $LaFe^+$ was synthesized and trapped in a background of argon at 4×10^{-6} torr. During the 5-s trapping time, the ions were irradiated with light from a 2.5-kW mercury–xenon arc lamp, used in conjugation with a series of cutoff filters.

$LaFe^+$ reacts readily with oxygen according to reaction 3, making the

$$LaFe^+ + O_2 \rightarrow LaO^+ + FeO \qquad (3)$$

background oxygen, even at system pressures of about 1×10^{-8} torr, a minor complication. Fortunately, LaO^+ is not reactive with alkanes[34] and its presence did not create a serious problem in this study.

Results and Discussion

Unimolecular Chemistry of $LaFe^+$. CID on $LaFe^+$ gives reaction 4 exclusively over the energy range studied (17–78 eV).

$$LaFe^+ \xrightarrow{\text{CID } 100\%} La^+ + Fe \qquad (4)$$

This result is expected from Stevenson's rule because of the large difference in the ionization potentials of lanthanum and iron (Fe, 7.870 eV; La, 5.577 eV).[30]

The bond energy $D°(La^+-Fe)$ was determined by photodissociation. $LaFe^+$ yields La^+ exclusively upon photodissociation. By using cutoff filters, the threshold for photodissociation was determined to be at about 590 nm, corresponding to $D°(La^+-Fe) = 48 \pm 5$ kcal/mol, which is the same as $D°(Sc^+-Fe)$ within experimental uncertainty.[20] This value also yields $D°(Fe^+-La) = 101 \pm 5$ kcal/mol and $\Delta H_f(LaFe^+) = 592$ kcal/mol.[35] A theoretical value of $D°(La-Fe) = 55$ kcal/mol has been reported,[1] which yields IP(LaFe) = 5.9 eV.

Reactions with Linear Alkanes. $LaFe^+$ reacts with all of the linear, branched, and cyclic alkanes employed in this study with the exception of methane. Dehydrogenation is by far the predominant reaction pathway, with carbon cleavage products observed only for a few cases. The rate constant for the reaction of $LaFe^+$ with propane was determined to be $4 \pm 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, corresponding to a reaction efficiency of 0.04. While ethane reacts somewhat slower than propane, other alkanes react at similar or slightly faster rates.

a. Methane, Ethane, and Propane. As is the case for its monoatomic counterparts, $LaFe^+$ does not react with methane. $LaFe^+$ does, however, react with ethane to form $LaFeC_2H_4^+$, reaction 5, suggesting that $D°(LaFe^+-C_2H_4) \geq 33$ kcal/mol.[35] Interestingly, the primary product ion undergoes sequential secondary reactions ultimately yielding $LaFe(C_2H_4)_4^+$. In contrast, Fe^+ is unreactive with ethane,[21] and while $LaC_2H_4^+$ is generated from La^+ and ethane, it does not undergo any secondary reactions with ethane.[34] CID of $LaFeC_2H_4^+$ at 22 eV gives both dehydrogenation and ethylene elimination products, as shown in reactions 6 and 7. Reaction 7 implies $D°(La^+-Fe) > D°(La^+-C_2H_4) \geq 33$ kcal/mol,[35] consistent with the measured $D°(La^+-Fe)$ value. The CID spectra of the secondary product ion $LaFe(C_2H_4)_2^+$ reveal some interesting features. At low energy (8 eV), CID gives a product distribution of 72% $LaFeC_4H_6^+$, 20% $LaFeC_4H_4^+$, and 8% $LaFeC_2H_4^+$, indicating that single and double dehydrogenations are facile processes. When the CID energy is increased, for example, to 31 eV, additional products are observed as shown in reactions 8–12. Reactions 8 and 10 suggest the successive loss of ethylene, consistent with a diethylene structure. However, the most convincing evidence for the presence of a diethylene–dimer ion structure is from the reaction of $LaFe(C_2H_4)_2^+$ with benzene, which gives 64% $LaFeC_6H_6^+$ and 36% $LaFe(C_2H_4)(C_6H_6)^+$. Reactions 11 and 12 may involve simple dehydrogenation or, conceivably, coupling processes may be involved to give ligands like cyclobutadiene and butadiene, respectively. As the energy is increased further, the bare cluster ion $LaFe^+$ emerges as the predominant product.

$$LaFe^+ + C_2H_6 \xrightarrow{100\%} LaFeC_2H_4^+ + H_2 \qquad (5)$$

$$LaFeC_2H_4^+ \xrightarrow{\text{CID } 22\%} LaFeC_2H_2^+ + H_2 \qquad (6)$$

$$\xrightarrow{78\%} LaFe^+ + C_2H_4 \qquad (7)$$

$$LaFe(C_2H_4)_2^+ \xrightarrow{\text{CID } 6\%} LaFe^+ + (2C_2H_4) \qquad (8)$$

$$\xrightarrow{9\%} LaFeC_2H_2^+ + (C_2H_6) \qquad (9)$$

$$\xrightarrow{29\%} LaFeC_2H_4^+ + C_2H_4 \qquad (10)$$

$$\xrightarrow{21\%} LaFeC_4H_4^+ + 2H_2 \qquad (11)$$

$$\xrightarrow{35\%} LaFeC_4H_6^+ + H_2 \qquad (12)$$

Propane reacts with $LaFe^+$ to yield $LaFeC_3H_6^+$ exclusively. Interestingly, as opposed to the secondary reactions observed in ethane, $LaFeC_3H_6^+$ only reacts very slowly to give an ion presumed to be the dimer–bispropene ion. The drastic reduction in the secondary reactivity compared to the ethane case is indeed puzzling. While the corresponding propene ion is observed for both Fe^+ and La^+, in contrast to $LaFe^+$, the former also gives iron–ethylene ion by elimination of methane, and the latter yields a multiple dehydrogenation product corresponding to allene lanthanum ion.[21,34]

Collision-induced dissociation of $LaFeC_3H_6^+$ at 51 eV yields a variety of product ions, reactions 13–20. Examination of these reactions reveals two series of fragmentations in the CID products. One series consists of those product ions which retain the heterodinuclear center, and the other series consists of those which have lost Fe. The complete absence of Fe^+ and Fe^+–ligand species is expected from the large IP difference between iron and lanthanum. The dimer ion series dominates at low collision energies (below about 26 eV), and the lanthanum ion series predominates at higher energies, a trend which in this study seems to be general for other $LaFe^+$–alkene ions. It is interesting to note that the lanthanum series is very similar to the CID results on La^+–propene generated from the reaction of La^+ with propane, suggesting that the $LaFeC_3H_6^+$ ion probably has a propene–dimer ion structure. Its displacement reaction with benzene yields $LaFeC_6H_6^+$, supporting the $LaFe^+$–propene structure.

$$LaFeC_3H_6^+ \xrightarrow{\text{CID } 3\%} La^+ + (Fe + C_3H_6) \qquad (13)$$

$$\xrightarrow{6\%} LaCH_2^+ + (Fe + C_2H_4) \qquad (14)$$

$$\xrightarrow{39\%} LaC_3H_2^+ + (Fe + 2H_2) \qquad (15)$$

$$\xrightarrow{5\%} LaC_3H_4^+ + (Fe + H_2) \qquad (16)$$

$$\xrightarrow{30\%} LaFe^+ + C_3H_6 \qquad (17)$$

$$\xrightarrow{2\%} LaFeC_2^+ + CH_4 + H_2 \qquad (18)$$

$$\xrightarrow{11\%} LaFeC_3H_2^+ + 2H_2 \qquad (19)$$

$$\xrightarrow{4\%} LaFeC_3H_4^+ + H_2 \qquad (20)$$

b. *n*-Butane. $LaFe^+$ reacts with normal butane to give single and double dehydrogenation products, reactions 21 and 22.

$$LaFe^+ + n\text{-}C_4H_{10} \xrightarrow{76\%} LaFeC_4H_6^+ + 2H_2 \qquad (21)$$

$$\xrightarrow{24\%} LaFeC_4H_8^+ + H_2 \qquad (22)$$

Observation of reaction 21, presumably to form a butadiene species, indicates $D°(LaFe^+-C_4H_6) \geq 56.5$ kcal/mol.[35] A secondary reaction forming an ion corresponding to $LaFe-C_8H_{14}^+$ was observed. From the slow secondary reaction of $LaFe^+$–

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[32] Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

[33] Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

[34] Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346.

[35] Rosenstock, H. M.; Draxl, D.; Steiner, R. W.; Heron, J. T. *J. Chem. Phys. Ref. Data, Suppl. 1* **1977**, *6*.

propene, the secondary reaction of $LaFeC_4H_8^+$ is expected to be very slow. Although it was difficult to obtain unambiguous double resonance ejection results, varying the reaction time clearly revealed a reactant–product relationship between $LaFeC_4H_6^+$ and the secondary product ion. In analogy to the $LaFe^+$–propene case, CID on $LaFeC_4H_6^+$ also gives two series of product ions: one series corresponds to the lanthanum butadiene ion and the other series consists of $LaFe^+$, $LaFeC_4H_2^+$, and $LaFeC_4H_4^+$, with the first series serving as a strong indication that the ion consists of a butadiene–$LaFe^+$ structure.

More interesting, however, are the CID results of the secondary product ion, $LaFeC_8H_{14}^+$. At low energy (8 eV), loss of H_2 to give $LaFeC_8H_{12}^+$ predominates. As the CID energy is increased, however, multiple dehydrogenation is observed, possibly proceeding by cyclization and coupling of the ligands. For example, the CID results of $LaFeC_8H_{14}^+$ at 40 eV are given in reactions 23–31. If

$$LaFeC_8H_{14}^+ \xrightarrow{\text{CID } 11\%} LaFeC_4^+ + (C_4H_{10} + 2H_2) \tag{23}$$

$$\xrightarrow{11\%} LaFeC_4H_2^+ + (C_4H_{10} + H_2) \tag{24}$$

$$\xrightarrow{16\%} LaFeC_4H_4^+ + (C_4H_{10}) \tag{25}$$

$$\xrightarrow{6\%} LaFeC_5H_4^+ + (C_3H_8 + H_2) \tag{26}$$

$$\xrightarrow{2\%} LaFeC_5H_6^+ + (C_3H_8) \tag{27}$$

$$\xrightarrow{30\%} LaFeC_6H_6^+ + (C_2H_6 + H_2) \tag{28}$$

$$\xrightarrow{8\%} LaFeC_8H_8^+ + 3H_2 \tag{29}$$

$$\xrightarrow{10\%} LaFeC_8H_{10}^+ + 2H_2 \tag{30}$$

$$\xrightarrow{6\%} LaFeC_8H_{12}^+ + H_2 \tag{31}$$

one postulates a bisbutadiene structure for the monodehydrogenation product ion in reaction 31, reaction 28 can be explained by a similar process observed for Fe^+–bisbutadiene,[36] $CuFe^+$–bisbutadiene,[25] and $CoFe^+$–bisbutadiene.[23] Upon CID, a metal-assisted Diels–Alder cycloaddition is proposed to occur forming a 4-vinylcyclohexene complex, followed by β-hydride shifts and the elimination of C_2H_4 and H_2 to form a benzene complex.

c. *n*-Pentane and *n*-Hexane. *n*-Pentane and *n*-hexane react with $LaFe^+$ to give the double dehydrogenation products $LaFeC_5H_8^+$ and $LaFeC_6H_{10}^+$, respectively. It is interesting to note that, although La^+ reacts with *n*-hexane to give mainly the triple dehydrogenation product $LaC_6H_8^+$,[34] the third hydrogen molecule is not lost in this case. In addition, Fe^+ reacts with these alkanes mainly by C–C insertion.[21]

CID of $LaFeC_5H_8^+$ at low energy (6 eV) yields 22% $LaFeC_5H_4^+$ and 78% $LaFeC_5H_6^+$, but at slightly higher energy (9 eV), fragmentation of the cluster ion to give $LaC_5H_6^+$ is also observed. Additional fragmentation is observed as the energy is increased further. For example, CID at 37 eV gives the fragments shown in reactions 32–35. Reaction 35 is similar to the CID features observed in La^+–cyclopentadiene,[34] and reactions 33–35 are similar to those observed for $LaFeC_5H_6^+$ generated from the double dehydrogenation of cyclopentane by $LaFe^+$, discussed later. Thus, these results suggest that dehydrocyclization of the linear pentadiene ligand may occur during the CID process.

$$LaFeC_5H_8^+ \xrightarrow{\text{CID } 4\%} LaFeC_5H_6^+ + H_2 \tag{32}$$

$$\xrightarrow{34\%} LaFeC_5H_4^+ + 2H_2 \tag{33}$$

$$\xrightarrow{44\%} LaC_5H_6^+ + (Fe + H_2) \tag{34}$$

$$\xrightarrow{18\%} LaC_5H_4^+ + (Fe + 2H_2) \tag{35}$$

The $LaFeC_6H_{10}^+$ ion generated from *n*-hexane was also studied by CID. Multiple dehydrogenation is very efficient at low energies. Its CID at 9 eV is shown in reactions 36–39. The observation of an abundant double dehydrogenation product ion in reaction 37 is again attributed to dehydrocyclization yielding a dimer-benzene ion. This notion is further supported by the fact that at higher energy (18 eV), the fragment $LaC_6H_6^+$ dominates, and at still higher energy (35 eV), $LaC_6H_4^+$, the principle CID fragment ion of lanthanum-benzene ion,[34] becomes important. In addition, CID on $LaFeC_6H_6^+$ formed from cyclohexane discussed later provides further evidence for this argument.

$$LaFeC_6H_{10}^+ \xrightarrow{\text{CID } 13\%} LaFeC_6H_8^+ + H_2 \tag{36}$$

$$\xrightarrow{64\%} LaFeC_6H_6^+ + 2H_2 \tag{37}$$

$$\xrightarrow{13\%} LaFeC_4H_4^+ + (C_2H_6) \tag{38}$$

$$\xrightarrow{10\%} LaC_6H_6^+ + (Fe + 2H_2) \tag{39}$$

Branched Alkanes. $LaFe^+$ reacts with branched alkanes in a manner similar to that with linear alkanes.

a. Isobutane. $LaFeC_4H_8^+$ is the only product observed for the reaction of $LaFe^+$ with isobutane. In contrast, La^+ doubly dehydrogenates isobutane to give lanthanum–trimethylenemethane ion,[31] while Fe^+ gives monodehydrogenation as well as methane elimination products.[21] The absence of the double dehydrogenation product ion, $LaFeC_4H_6^+$, suggests that 1,3-dehydrogenation is not as favorable for $LaFe^+$ as it is for La^+. Although extremely slow, the primary product ion reacts further to give $LaFe(C_4H_8)_2^+$ at extended trapping times. CID of the $LaFe^+$–isobutene ion at 38 eV gives the results in eq 40–43. These CID results are readily distinguishable from that of the isomeric ion, $LaFe(C_2H_4)_2^+$, indicating that the isobutene does not rearrange to the diethylene structure following activation and vice versa.

$$LaFe^+\text{–isobutene} \xrightarrow{\text{CID } 44\%} LaC_4H_6^+ + (Fe + H_2) \tag{40}$$

$$\xrightarrow{26\%} LaFe^+ + C_4H_8 \tag{41}$$

$$\xrightarrow{11\%} LaFeC_4H_4^+ + 2H_2 \tag{42}$$

$$\xrightarrow{19\%} LaFeC_4H_6^+ + H_2 \tag{43}$$

b. Neopentane. $LaFe^+$ reacts with neopentane at a somewhat lower rate than with all of the other alkanes except methane. Both dehydrogenation and methane elimination products are observed, reactions 44 and 45. Because of the lack of β-hydrogens following initial C–H insertion, reaction 45 probably involves 1,3-dehydrogenation, a mechanism common in reactions of group 3 metal ions with alkanes.[34,37] However, the obvious decrease in reaction rate indicates that 1,3-dehydrogenation is not a very favorable initiation step, consistent with the results of $LaFe^+$ with isobutane discussed above. Considering that C–C bond insertion is not commonly observed for $LaFe^+$ reacting with alkanes, reactions 44 and 45 may proceed by initial insertion of the metal center into a C–H bond, followed by either a 1,3-dehydrogenation yielding β,β-dimethylmetallocyclobutane ion with the dimer ion as the metallocenter or a 1,2-methane elimination giving $LaFe^+$–isobutene. C–C insertion, however, cannot be completely ruled out. CID of $LaFeC_4H_8^+$ obtained from reaction 44 is identical with that of $LaFe^+$–isobutene from the reaction of $LaFe^+$ with isobutane within experimental error, supporting the 1,2-methane elimination mechanism. CID of $LaFeC_5H_{10}^+$ from reaction 45 gives two major fragments, $LaFeC_4H_6^+$ and $LaC_5H_6^+$, with the former predominating at lower energy (8 eV) and the latter predominating at somewhat higher energy (18 eV). Lack of a simple dehydrogenation fragment from CID indicates that the ion does not have a linear structure, as predicted. These results suggest that $LaFeC_5H_{10}^+$ fragments initially by loss of methane to give an ion probably corresponding to $LaFe^+$–trimethylenemethane which, if excess energy is available, can fragment further

$$LaFe^+ + \text{neopentane} \xrightarrow{70\%} LaFeC_4H_8^+ + CH_4 \tag{44}$$

$$\xrightarrow{30\%} LaFeC_5H_{10}^+ + H_2 \tag{45}$$

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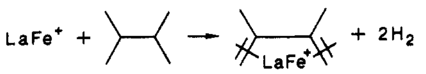
(36) Jacobsen, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

(37) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492.

by loss of Fe. A similar mechanism was proposed for the reaction of La^+ with neopentane,[34] only in that case the *β,β*-dimethyllanthanocyclobutane intermediate ion is not a stable product and fragments directly to La^+–trimethylenemethane.

c. 2,3-Dimethylbutane. $LaFe^+$ reacts with 2,3-dimethylbutane to form $LaFeC_6H_{10}^+$ exclusively. The reaction probably proceeds by successive 1,2-dehydrogenations to give $LaFe^+$–2,3-dimethyl-1,3-*cis*-butadiene as shown in reaction 46, implying



(46)

$D°(LaFe^+–C_6H_{10}) \geq 53.9$ kcal/mol.[35] The primary product ion reacts further to give $LaFe(C_6H_{10})_2^+$. It is interesting to note that the butadiene–dimer ion also gave a secondary reaction with *n*-butane, although only by single dehydrogenation. CID of the $LaFeC_6H_{10}^+$ ion at 9 eV gives the monodehydrogenation product only. Other fragments, however, appear at higher energy. For example, its CID at 18 eV gives the product distribution in reactions 47–50. At still higher energy (35 eV), $LaC_6H_6^+$ becomes the predominant peak and reaction 48 also becomes more important. Although the product ions are similar to those observed for $LaFeC_6H_{10}^+$ from *n*-hexane, reactions 36–39, the difference in relative intensities suggests that these two ions do not have the same structure.

$$LaFeC_6H_{10}^+ \xrightarrow{\text{CID } 11\%} LaC_6H_6^+ + (Fe + 2H_2) \quad (47)$$

$$\xrightarrow{2\%} LaFeC_4H_4^+ + C_2H_6 \quad (48)$$

$$\xrightarrow{10\%} LaFeC_6H_6^+ + 2H_2 \quad (49)$$

$$\xrightarrow{77\%} LaFeC_6H_8^+ + H_2 \quad (50)$$

Cyclic Alkanes. a. Cyclopropane. Cyclopropane is an interesting example where C–C bond cleavage is observed, reactions 51 and 52. The reaction probably proceeds by initial insertion of the metal center into the strain-weakened C–C bond. This metallocycle can then either ring-open to an ethene–methylidene structure or, by hydrogen transfer, generate an allyl–hydride species. The ethene–methylidene ion decomposes by eliminating methane to give presumably $LaFe^+$–acetylene, while transfer of the allylic hydrogen and elimination of H_2 yields presumably $LaFe^+$–allene. Reactions 51 and 52 imply that $D°(LaFe^+–\text{acetylene}) \geq 23.6$ kcal/mol and $D°(LaFe^+–\text{allene}) \geq 33.2$ kcal/mol.[30] CID of $LaFe^+$–allene at 41 eV yields products as shown in reactions 53–56. The monodehydrogenation process, reaction 53, becomes more important at lower energy and is the only fragment observed at 11 eV. Given that the CID of $LaFe^+$–propene proceeds via dehydrogenation yielding $LaFe^+$–allene as an intermediate, features from the CID of $LaFe^+$–allene should resemble that of $LaFe^+$–propene and this is indeed the case.

$$LaFe^+ + \text{cyclopropane} \xrightarrow{38\%} LaFeC_2H_2^+ + CH_4 \quad (51)$$

$$\xrightarrow{62\%} LaFeC_3H_4^+ + H_2 \quad (52)$$

$$LaFe^+\text{–allene} \xrightarrow{\text{CID } 48\%} LaFeC_3H_2^+ + H_2 \quad (53)$$

$$\xrightarrow{5\%} LaFeC_2^+ + CH_4 \quad (54)$$

$$\xrightarrow{20\%} LaC_3H_4^+ + Fe \quad (55)$$

$$\xrightarrow{27\%} LaC_3H_2^+ + (Fe + H_2) \quad (56)$$

b. Cyclobutane. Cyclobutane reacts with $LaFe^+$ as shown in reactions 57–59. Considering the preference of $LaFe^+$ for C–H over C–C bond insertion, the reactions of $LaFe^+$ with cyclobutane may proceed by successive dehydrogenation to give $LaFe^+$–cyclobutene and $LaFe^+$–cyclobutadiene. A similar mechanism was also suggested for the reaction between La^+ with cyclobutane.[34] However, in the absence of conclusive structural evidence for the product ions, reactions 57–59 can also be explained by a mechanism involving insertion of the cluster ion into a strain-weakened C–C bond yielding a metallocyclopentane intermediate ion, which subsequently decomposes. This mechanism has been proposed for the reactions of group 8 transition metal ions with cyclobutane.[37] CID of $LaFe^+–C_4H_4$ at 41 eV yields the results shown in reactions 60–63. The monodehydrogenation process, reaction 60, predominates at lower energy. Unfortunately, these data do not provide conclusive structural evidence.

$$LaFe^+ + \text{cyclobutane} \xrightarrow{12\%} LaFeC_2H_4^+ + C_2H_4 \quad (57)$$

$$\xrightarrow{68\%} LaFeC_4H_4^+ + 2H_2 \quad (58)$$

$$\xrightarrow{20\%} LaFeC_4H_6^+ + H_2 \quad (59)$$

$$LaFeC_4H_4^+ \xrightarrow{\text{CID } 50\%} LaFeC_4H_2^+ + H_2 \quad (60)$$

$$\xrightarrow{7\%} LaFeC_2H_2^+ + C_2H_2 \quad (61)$$

$$\xrightarrow{31\%} LaC_4H_2^+ + (Fe + H_2) \quad (62)$$

$$\xrightarrow{12\%} LaC_2H_2^+ + (Fe + C_2H_2) \quad (63)$$

c. Cyclopentane. $LaFe^+$ reacts with cyclopentane to give the double dehydrogenation product $LaFeC_5H_6^+$, exclusively, indicating that $D°(LaFe^+–\text{cyclopentadiene}) > 50.5$ kcal/mol.[35] Secondary reactions to give $LaFe(C_5H_6)_2^+$ and $LaFe(C_5H_6)(C_5H_8)^+$, although somewhat slow, were observed. CID of the primary ion at 30 eV gives reactions 64–68. The CID fragment ions which have lost an Fe atom are similar to those observed from CID of lanthanum–cyclopentadiene ion,[34] supporting the cluster–cyclopentadiene structure.

$$LaFeC_5H_6^+ \xrightarrow{\text{CID } 3\%} LaC_3H_4^+ + (Fe + C_2H_2) \quad (64)$$

$$\xrightarrow{11\%} LaC_5H_4^+ + (Fe + H_2) \quad (65)$$

$$\xrightarrow{27\%} LaC_5H_6^+ + Fe \quad (66)$$

$$\xrightarrow{8\%} LaFeC_4H_4^+ + CH_2 \quad (67)$$

$$\xrightarrow{51\%} LaFeC_5H_4^+ + H_2 \quad (68)$$

d. Cyclohexane and Methylcyclohexane. Both alkanes react with $LaFe^+$ by dehydrogenation exclusively, giving presumably $LaFe^+$–benzene and $LaFe^+$–toluene, respectively, and implying $D°(LaFe^+–\text{benzene}) \geq 49.3$ kcal/mol and $D°(LaFe^+–\text{toluene}) \geq 48.9$ kcal/mol.[35] CID of the former product ion at 28 eV gives 20% $LaFe^+$, 68% $LaC_6H_6^+$, and 12% $LaC_6H_4^+$, consistent with the $LaFe^+$–benzene structure. The predominance of $LaC_6H_6^+$ ion suggests $D°(La^+–Fe) < D°(La^+–C_6H_6) = 58 \pm 8$ kcal/mol,[38] which is consistent with $D°(La^+–Fe) = 48 \pm 5$ kcal/mol determined by photodissociation. Finally, benzene is observed to displace Fe in $LaFe^+$ to form La^+–benzene, in accord with the above conclusion. CID of the primary product from methylcyclohexane at 27 eV yields 17% $LaFe^+$ and 83% $LaC_7H_8^+$, consistent with a $LaFe^+$–toluene structure.

Conclusion

In accordance with the trend observed from studies in our laboratory on the properties of heterodinuclear metal cluster ions and their constituent monoatomic metal ions, the reactivity of $LaFe^+$ is quite different from that of either La^+ or Fe^+. In particular, it is worth pointing out that group 3 transition metal ions are peculiar in forming M^+–dialkyl ions with many linear and branched alkanes larger than propane, such as *n*-butane and isobutane.[34,39] In contrast, no dialkyl product ions are observed from $LaFe^+$ with the alkanes. This can be attributed to the cluster ion preference of C–H insertion over C–C insertion, with the latter step necessary in forming a dialkyl metal product ions.

Interestingly, while other dinuclear ions, such as VFe^+,[24] $CoFe^+$,[23] and $NbFe^+$,[40] and $CuFe^+$,[25] distinguish themselves from

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(38) Lech, L. M.; Huang, Y.; Freiser, B. S., unpublished results.

(39) Tolbert, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 8117.

their constituent monoatomic metal ions by showing no appreciable reactivity toward alkanes, LaFe$^+$ is reasonably reactive with alkanes. Simple dehydrogenation predominates its reactions with alkanes, while alternative pathways are possible when such dehydrogenation is blocked. Neopentane, for example, reacts with LaFe$^+$ to give both methane elimination and 1,3-dehydrogenation product ions. Carbon–carbon cleavage is a dominant process in the reaction of LaFe$^+$ with cyclopropane, which has its origin in the large ring strain.

Generally two series of CID product ions are formed by CID on LaFe$^+$–alkene ions. One series of fragments retain the dimer center and predominates at lower energy, and the other series arising from loss of Fe atom predominates at higher energy and resembles the CID spectra of the analogous La$^+$ complex. While CID of all of the LaFe$^+$–alkene ions studied tends to give a wide variety of fragment ions, two fragments in particular appear quite frequently. Not surprisingly, one of these fragments is LaFeC$_6$H$_6^+$ because of the special stability of benzene. For example, coupling of the two ligands in reaction 28 and dehydrocyclization in reaction 37 to give LaFeC$_6$H$_6^+$ are both efficient processes. More surprising, however, is the frequency in which LaFeC$_4$H$_4^+$ is observed as a CID product. Although additional studies will be necessary to draw definitive conclusions, one interesting possibility is that the ion has a LaFe$^+$–cyclobutadiene structure. There currently exist ample examples where a transition metal center can greatly stabilize the otherwise elusive cyclobutadiene species.[41]

The reactivity of LaFe$^+$ with saturated hydrocarbons is in contrast to the lack of reactivity observed on previously studied metal dimer ions. Preliminary results from our laboratory, however, indicate that RhFe$^+$ and RhCo$^+$ also react with alkanes.[27] Because of the lack of a comprehensive understanding of the metal–metal interaction for even simple dinuclear transition metal dimer ions at this stage, rationalization of the reactivities in terms of metal–metal bonding and other factors is difficult, if not impossible. Understanding or predicting such reactivities will require more theoretical and experimental study in this field.

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Registry No. La$^+$, 14175-57-6; Fe(CO)$_5$, 13463-40-6; LaFe$^+$, 111496-23-2; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; *n*-butane, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; isobutane, 75-28-5; neopentane, 463-82-1; 2,3-dimethylbutane, 79-29-8; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2.

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(40) Buckner, S. W.; Freiser, B. S., paper in preparation.

(41) Efraty, A. *Chem. Rev.* **1977**, *77*, 691.

Interaction of Adenosine 5′-Triphosphate with Mg^{2+}: Vibrational Study of Coordination Sites by Use of ^{18}O-Labeled Triphosphates

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Abstract: Infrared and Raman spectra were measured of ATP and its three isotopomers whose triphosphate oxygen atoms were selectively substituted by ^{18}O. The observed frequency shifts on ^{18}O-substitution made it possible to determine the contributions of each phosphate group (α, β, or γ) to the infrared and Raman bands. Several infrared bands of ATP or ^{18}O-labeled ATP were found to be assignable to vibrations predominantly involving one of the three phosphate groups. Frequency shifts of such localized vibrations on complex formation are useful to investigate the sites of coordination of Mg^{2+} to ATP. At pH 3.0, comparable frequency shifts were observed for the vibrations localized at individual PO$_2^-$ groups together with intensity changes of main chain vibrations attributable to conformational isomerization in some of the ATP molecules. These infrared data can be interpreted as due to coexistence of α,β-, β,γ-, and α,γ-bidentates. At pH 7.5, an α-PO$_2^-$ vibration shifted by the same frequency as that at pH 3.0, whereas β-PO$_2^-$ vibrations showed twice as large shifts as those at pH 3.0. A similarly strong interaction of Mg^{2+} with γ-PO$_3^{2-}$ was also suggested by the frequency shift data. MgATP at pH 7.5 is, thus, supposed to be a mixture of β,γ-bidentate and α,β,γ-tridentate complexes. Implications of the present findings for enzymatic reactions involving MgATP are discussed.

Adenosine 5′-triphosphate (ATP) is an energy transfer agent in biological systems, and the enzymatic reactions involving ATP usually require divalent cations, most often Mg^{2+}, as cofactors. Because of the relatively high concentration of Mg^{2+} in living cells and the high affinity of ATP for the cation, ATP largely exists as the 1:1 MgATP complex,[1] and such complexes are real substrates of some enzymatic reactions.[2]

Interactions of ATP with Mg^{2+} in aqueous solution have been studied intensively by spectroscopic methods, which have commonly shown that the adenine ring of ATP is not, or only negligibly, involved in the interactions with Mg^{2+}, but the triphosphate moiety interacts with the cation.[3-5] However, there is no agreement about which of the three phosphate groups (α, β, and γ) is involved in the Mg^{2+} coordination. ^{31}P NMR studies proposed several models for MgATP: β-monodentate,[6] β,γ-biden-

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(1) Frey, C. M.; Stuehr, J. E. *J. Am. Chem. Soc.* **1972**, *94*, 8898–8904.
(2) Cleland, W. W. *Annu. Rev. Biochem.* **1967**, *36*, 77–112.
(3) Cohn, M.; Hughes, T. R., Jr. *J. Biol. Chem.* **1962**, *237*, 176–181.
(4) Happe, A. J.; Morales, M. *J. Am. Chem. Soc.* **1966**, *88*, 2077–2078.
(5) Lanir, A.; Yu, N. T. *J. Biol. Chem.* **1979**, *254*, 5882–5887.
(6) Tran-Dinh, S.; Roux, M.; Ellenberger, M. *Nucleic Acids Res.* **1975**, *2*, 1101–1110.

0002-7863/88/1510-0392$01.50/0