thesis of uniformly ^{13}C labeled RNAs of defined sequence are quite general. The RNA duplex was generated by in vitro transcription with T7 RNA polymerase[11] using isotopically labeled nucleotide triphosphates (NTPs). The labeled NTPs were prepared by extracting ribosomal RNA from *Escherichia coli* grown on 99% ^{13}C enriched media, degrading the RNA to NMPs and enzymatically synthesizing the NTPs.[12,13] These techniques allow production of milligram quantities of isotopically labeled RNA oligomers of defined sequence.

In conclusion, we have shown how a 4D heteronuclear NMR experiment can enormously facilitate the resonance assignment and structural analysis of RNA. The tremendous increase in resolution in the 4D NMR experiment will allow detailed structure determination of much larger RNAs than previously has been possible.

Acknowledgment. We thank Dr. D. Fry and Hoffmann-La Roche for use of their NMR to run the 4D experiment, Drs. L. Mueller and M. Gorlach for providing isotopically labeled *E. coli*, and A. Sirr and L. Baer for assistance in preparation of the isotopically labeled NTPs. This work was supported in part by NIH AI 30726, and we also thank the W. M. Keck Foundation for their generous support of RNA science on the Boulder campus.

Registry No. r(GGCGCUUGCGUC), 138153-87-4.

Supplementary Material Available: Details on the pulse sequence and processing parameters used in the 4D HMQC–NOE–HMQC experiment along with additional figures illustrating the improved resolution of the H1′/H5′ region of the RNA duplex in this 4D experiment (4 pages). Ordering information is given on any current masthead page.

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Reactions of State-Selected Co^+ with C_3H_8

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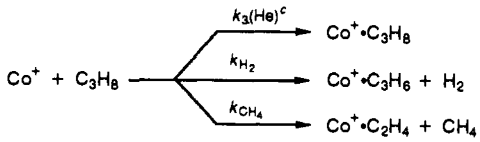
The growing use of mass spectrometric techniques for probing the kinetics, dynamics, and thermochemistry of transition-metal reactions has shown these reactions to be complex and usually extremely dependent on the metal ion electronic state.[1-10] Consequently, knowledge of state-specific reactions for these ions is especially important. Recently, we have developed a "chromatographic" technique to determine the electronic-state distribution present in transition-metal ions.[1] This allows us to study state-selected reactions. In this communication, we report the quantitative determination of rate constants and branching ratios for state-selected Co^+ reacting with propane. Observed rates for adduct formation as well as H_2 and CH_4 elimination channels were found to depend strongly on the electronic configuration of the metal ion.

Table I. Rate Constants for the Reactions[a,b]



	$k_3{}^d$	$k_{H_2}{}^d$	$k_{CH_4}{}^d$	k_{H_2}/k_{CH_4}
Co^+ (^3F, $3d^8$)	48	0.69	0.15	4.7
$(Co^+)^*$ (^3F, $4s3d^7$)	1.3	2.5	2.8	0.9
$k_{Co^+}/k_{(Co^+)^*}$	37	0.28	0.05	

[a] The accuracy of the absolute rate coefficient measurements is estimated to be within ±30%.[11] The relative rate coefficient measurements, however, are much more accurate. [b] The pressure of propane was varied from 1×10^{-5} to 4×10^{-5} Torr, yielding rate constants within ±15%. [c] Only He stabilization is important due to the low propane pressure. [d] 10^{-11} cm^3/s.

Details of the experimental apparatus have been published.[11] In experiments reported here, cobalt ions are formed by electron impact on $Co(CO)_3NO$ and $CoCp(CO)_2$ in the ion source of a double-focusing mass spectrometer. The Co^+ ions are mass selected and injected (with 2–3 eV of translational energy) into a high-pressure drift cell. The ions are quickly thermalized by collisions with He (P_{He} = 2 Torr) and react with a trace of C_3H_8 (4×10^{-5} Torr). A small electric field drifts the ions through the cell ($E/N < 4$ Td). Ions exit the cell, are passed through a quadrupole mass filter, and are detected.

Ion arrival time distributions (ATDs) are measured by pulsing the mass-selected ions into the drift cell (pulse width ≈ 1–3 μs). The pulse simultaneously triggers a time-to-pulse-height converter ramp. Ions that exit the cell are then collected as a function of time, yielding the ATD. Ions that have different mobilities have different drift times through the cell and appear as different peaks in the ATD. The ATD for Co^+ is bimodal, corresponding to ground ($3d^8$) and excited ($4s3d^7$) electronic state configurations.[1] The 4s-containing state of Co^+ is larger and more repulsive than the state containing only 3d electrons. This reduced attraction gives the excited-state Co^+ a 50% greater mobility than the ground state. The electronic-state populations are a function of both the electron energy and the neutral precursor used. For example, at 50 eV, electron impact on $Co(CO)_3NO$ produces 36% ground-state Co^+, whereas $CoCp(CO)_2$ produces 83% ground-state Co^+.

Once the electronic-state population of Co^+ is known, relative rates of ground- and excited-state Co^+ reacting with propane are obtained as follows. Propane is added to the drift cell, and the fractional decrease $[Co^+]/[Co^+]_0$ is measured as a function of time to obtain the total rate constant, k. Under the low conversion conditions in our experiment, the exponential decays of both ground- and excited-state Co^+ are well-described by linear functions. Thus, the sum of these two exponentials effectively reduces to a single exponential decay:

$$\frac{Co^+}{(Co^+)_0} = e^{-kt} \tag{1}$$

where $k = fk_{gs} + (1 - f)k_{ex}$. Co^+ corresponds to the sum of ground- and excited-state Co^+, f is the fraction of ground-state

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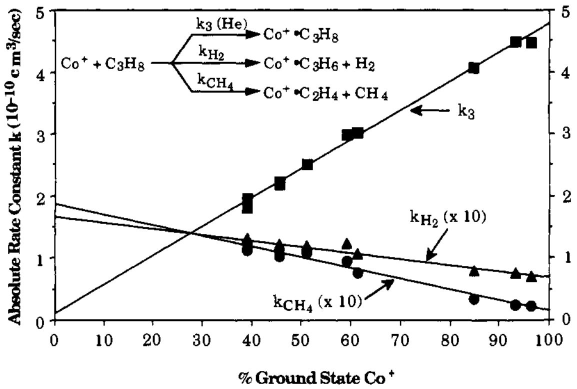

Figure 1. Absolute rate constants for $Co^+C_3H_8$ adduct formation and for H_2 and CH_4 elimination channels as a function of % ground-state Co^+. The linear least-square fit of the experimental data points is used to extrapolate to rates of reaction corresponding to 100% ground-state and 100% excited-state Co^+.[12]

Co^+, and k_{gs} and k_{ex} are the ground- and excited-state rate constants, respectively. We obtain k by plotting ln $Co^+/(Co^+)_0$ versus time.[12] We measure k as a function of % ground-state Co^+ and extrapolate to 100% ground-state ($f = 1$) and 100% excited-state Co^+ ($f = 0$) to determine the individual total rates of reaction. Product distributions are then also measured as a function of % ground-state Co^+ to obtain individual rate constants (Table I).

The rate of adduct formation as a function % ground-state Co^+ is shown in Figure 1. The experimental data points range from 38 to 96% ground-state Co^+. The linear least-squares fit of the data indicates that for 100% ground-state Co^+ (a^3F $3d^8$) the rate of adduct formation is 4.7×10^{-10} cm^3 s^{-1}, which is approximately 40 times greater than for the b^3F $4s3d^7$ state.[13] The repulsive 4s electron in the excited state is responsible for the greatly reduced clustering efficiency with propane.

The H_2 and CH_4 elimination channels are relatively minor for ground-state Co^+ in our high-pressure experiment, approximately two orders of magnitude smaller than the rate for adduct formation. These elimination channels are greatly enhanced for the electronically excited Co^+ as shown in Figure 1. The inefficiency of H_2 and CH_4 elimination for ground-state Co^+ reacting with propane has been shown to be due to the initial C–H bond activation transition state, which is rate-limiting.[16] This transition state was found to be located only 0.11 eV below the Co^+/C_3H_8 asymptotic energy. As a result, the vibrationally excited $CoC_3H_8^+$ complex can dissociate back to reactants or can be collisionally stabilized in competition with elimination channels.

The branching ratio for H_2 and CH_4 elimination, $k(H_2)/k(CH_4)$, is 4.7 for ground-state and 0.9 for excited-state Co^+ reacting with C_3H_8. The most plausible explanation for the dramatic increase in CH_4 elimination for the excited-state Co^+ is that both C–C and C–H bond activation are occurring on the excited-state surface, while only C–H bond activation occurs on the ground-state surface. The ratio of 4.7 for ground-state Co^+ is in good agreement with the results obtained by Armentrout et al.[11] and Tonkyn et al.[17] which are 3.3 and 3.0, respectively. This ratio is very sensitive to the presence of minor amounts of excited-state Co^+. Laser vaporization produces at least a few percent excited-state Co^+.[18] Correcting for an assumed 2% excited-state contribution in the laser vaporization results of Tonkyn et al. would increase the branching ratio from 3.0 to 4.0. This relatively large correction for a small percent excited-state population emphasizes the fact that the excited-state contribution to reactivity studies of transition-metal ions must be taken into consideration.

In summary, the new electronic-state chromatography technique allows the measurement of state-selected bimolecular rate constants of transition-metal ions at thermal translational energies. A much more complete account of the method and its application to the interesting Fe^+/propane system will be published shortly.[19]

Acknowledgment. The support of the National Science Foundation under grant CHE 88-17201 is gratefully acknowledged.

Note Added in Proof. Surface ionization experiments were done to determine the reactivity of the Co^+ a^5F first excited state. Surface ionization of $CoCl_2$ produced 15% a^5F $4s3d^7$ and 85% a^3F $3d^8$ ground state. The a^5F $4s3d^7$ state reacted with propane at about the same rate as the $4s3d^7$ electronic configuration(s) formed by electron impact. The b^3F $4s3d^7$ second excited state is known to be formed by electron impact on $Co(CO)_3NO$.[1,14] How much, if any, of the a^5F $4s3d^7$ first excited state is formed by electron impact has yet to be determined. However, the presence of any Co^+ a^5F should have a negligible effect on our reported Co^+ b^3F + C_3H_8 rate due to the similar reactivity of the two states.

Registry No. Co^+, 16610-75-6; C_3H_8, 74-98-6.

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(12) The time used in the analysis corresponds to ground-state Co^+. The extrapolated rate constant for excited-state Co^+ (0% ground state in Figure 1) is corrected for the shorter reaction time for excited-state Co^+. These corrected values are listed in Table I.

(13) The b^3F $4s3d^7$ second excited state is known to be formed by electron impact on $Co(CO)_3NO$.[1,14] Fisher et al.[15] have observed the a^5F $4s3d^7$ first excited state using surface ionization. Electron impact may form the a^5F state as well. See Note Added in Proof.

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Reagent-Based Stereocontrol in Formation of Substituted Tetrahydrofurans

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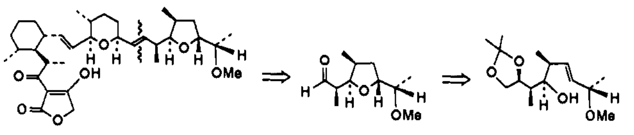
In planning an approach to the tetrahydrofuran (THF) portion (**2**)[1] of tetronasin (**1**)[2] utilizing our reiterative method for polypropionate constructions,[3] the key transformation was anticipated to be an electrophilic ring closure of a chiral, nonracemic homoallylic alcohol, **3**. Although cyclizations of related substrates with the goal of controlling stereochemical relationships in particular between the 2- and 5-positions have begun to attract attention,[4]



1 tetronasin **2** **3**

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