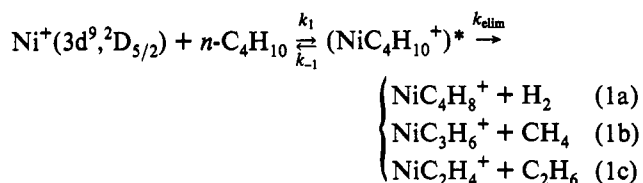# Bimolecular Reactions in Real Time: $Ni^+(^2D_{5/2})$ + n-C$_4$H$_{10}$ Elimination Reactions

Robert J. Noll and James C. Weisshaar*

Department of Chemistry
University of Wisconsin—Madison
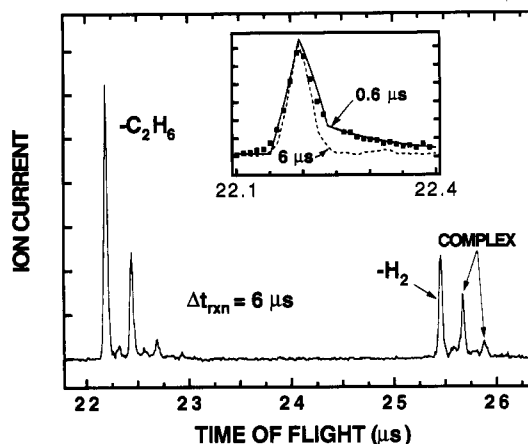Madison, Wisconsin 53706-1396

We report a new probe of ion–molecule reaction dynamics that directly measures the time evolution of *bimolecular* collision complexes under single collision conditions with 100-ns time resolution. The technique provides a model-independent test of statistical theories as applied to the decay of ion–molecule collision complexes. The reaction is[1-3]

$$Ni^+(3d^9, {}^2D_{5/2}) + n\text{-}C_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NiC_4H_{10}^+)^* \overset{k_{elim}}{\rightarrow}$$

$$\begin{cases} NiC_4H_8^+ + H_2 & (1a) \\ NiC_3H_6^+ + CH_4 & (1b) \\ NiC_2H_4^+ + C_2H_6 & (1c) \end{cases}$$

A neutral atomic Ni beam, a molecular beam of n-C$_4$H$_{10}$, and a 7-ns dye laser pulse at 30 923 cm^{-1} cross in field-free space.[4] At $t = 0$, the laser creates $Ni^+(^2D_{5/2})$ by resonant two-photon ionization,[5,6] and formation of $(NiC_4H_{10}^+)^*$ collision complexes begins. After an adjustable reaction time Δt_{rxn} of 0–8 μs, a pulsed electric field accelerates all ions (extraction time 2 μs at $m/e = 116$) for mass analysis by time-of-flight over a 1-m field-free path. Such mass spectra provide time-resolved snapshots of the evolution of bimolecular collision complexes forward to elimination products or back to reactants.

At 0.2 kcal mol^{-1} collision energy, the experiment reveals three distinct collision pathways. We estimate the absolute reaction cross section to be roughly 40% of the Langevin cross section, in sensible agreement with earlier ion beam work at higher collision energies.[1b,2] Thus we infer that about 60% of the Langevin collisions return promptly to reactants in less than 100 ns. Another 35% of collisions form long-lived $(NiC_4H_{10}^+)^*$ complexes that evolve to elimination products on a 400-ns time scale. The remaining 5% of collisions form "frustrated complexes" that live ~10 μs.

Figure 1 shows a product time-of-flight mass spectrum (TOF-MS) for $\Delta t_{rxn} = 6$ μs. The product branching fractions are 63% C$_2$H$_6$ elimination, 1% CH$_4$ elimination, 26% H$_2$ elimination, and 11% NiC$_4$H$_{10}^+$ complexes. The peaks from all three products appear comparably narrow for large reaction times. At $\Delta t_{rxn} = 0.6$ μs (inset, Figure 1), the NiC$_2$H$_4^+$ peak (C$_2$H$_6$ elimination) clearly exhibits a *tail* toward long times. The tail is due to

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(6) Ni$^+$ is formed exclusively in the ground spin–orbit level $^2D_{5/2}$, the only level energetically accessible by R2PI at 30 923 cm^{-1}.

Figure 1. Product mass spectrum for $Ni^+(^2D_{5/2})$ + n-C$_4$H$_{10}$ at $\Delta t_{rxn} = 6$ μs and $E_{coll} = 0.2$ kcal mol^{-1}. Peaks from 22–23 μs are isotopes of NiC$_2$H$_4^+$ (+C$_2$H$_6$) product. Peak at 25.5 μs is entirely ^{58}NiC$_4$H$_8^+$ (+H$_2$). Peaks at 25.7 and 25.9 μs are predominantly ^{58,60}NiC$_4$H$_{10}^+$ complexes. Inset shows expanded view of ^{58}NiC$_2$H$_4^+$ (+C$_2$H$_6$) peak for $\Delta t_{rxn} = 6$ (dashed) and 0.6 μs (squares). The solid line is a fit that assumes a single exponential decay with $\tau = 400$ ns; the distribution of times between formation of a complex and extraction of the ions at Δt_{rxn} is properly accounted for.

NiC$_4$H$_{10}^+$ complexes that fragment to NiC$_2$H$_4^+$ *while accelerating*, as commonly observed in the metastable decay of fragment ions in photoionization.[7] A single exponential decay with 400 ± 100-ns lifetime fits both the narrow component and the tail of the NiC$_2$H$_4^+$ peak quite well (inset, solid line). The model used to fit the data properly averages over the distribution of times at which complexes are born between $t = 0$ and Δt_{rxn}. The ±100-ns error limits give the range of assumed lifetimes that produce plausible fits to the data. The leading edges of the 50-ns rise time, kilovolt pulses applied to the extraction plates must coincide within 5 ns in order to obtain undistorted metastable tail shapes. Simulations suggest we could just discern the tail due to a 100-ns decay process.

We have carried out exhaustive tests to check that the tail is not an experimental artifact due to too large a number density of Ni$^+$ (which could cause space–charge effects) or too large a number density of Ar or C$_4$H$_{10}$ (which could cause unwanted collision-induced dissociation during extraction of the ions). The tail is robust and behaves as expected over a wide range of reaction times and number densities.

As Δt_{rxn} increases beyond 1 μs, which is several times the 400 ns lifetime, the absolute amplitude of the tail reaches steady state, as the sequential mechanism of eq 1 predicts. Meanwhile, the amplitude of the *narrow* component of NiC$_2$H$_4^+$, which is due to products born prior to extraction, increases linearly with time, as expected. Thus the overall NiC$_2$H$_4^+$ peak appears quite narrow for $\Delta t_{rxn} = 6$ μs. The NiC$_4$H$_8^+$ peak (H$_2$ elimination) lacks a discernible tail because its mass is so similar to that of NiC$_4$H$_{10}^+$. The constant ratio of NiC$_4$H$_8^+$ to NiC$_2$H$_4^+$ intensity for all $\Delta t_{rxn} \geq 100$ ns indicates that H$_2$ and C$_2$H$_6$ elimination occur on the *same time scale*.

The appearance of NiC$_4$H$_{10}^+$ in the TOF-MS at $\Delta t_{rxn} = 6$ μs shows that a second type of complex survives much longer than 400 ns. The NiC$_4$H$_{10}^+$ peaks are distorted toward *shorter* time due to fragmentation of complexes after extraction but before detection (2–25 μs). The strong electric field near the detector causes these delayed fragments to arrive slightly *earlier* than the remaining complexes. In a separate set of experiments, we have intentionally applied a strong, retarding axial electric field between the extraction and detection regions.[8] We can thereby completely

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separate the delayed fragments from the remaining complexes and determine the fragment masses. The flight times show that the metastable fragments include both Ni^+ ($+C_4H_{10}$) and $NiC_2H_4^+$ ($+C_2H_6$). The structure of these frustrated complexes is unknown.

At 5 kcal mol^{-1} collision energy, the absolute reaction efficiency remains ~40%. At $\Delta t_{rxn} = 8$ μs, we observe 55% C_2H_6 elimination, 1% CH_4 elimination, 26% H_2 elimination, and 19% $NiC_4H_{10}^+$ complexes with lifetimes of 2–25 μs. The $NiC_2H_4^+$ peak again tails toward longer time. The lifetime remains 400 ± 100 ns at the higher energy.

Clues to the mechanism of the reaction at low collision energy come from previous ion beam studies.[2,3] Most revealing is the remarkably specific product distribution from Ni^+ + *n*-butane-*1,1,1,4,4,4-d₆*. At 0.5-eV kinetic energy, all of the hydrogen elimination channel is $NiC_4H_4D_4^+$ + D_2, *i.e.*, 1,4-elimination dominates. For the ethane elimination channel, the products are >95% $NiC_2H_2D_2^+$ + $C_2H_2D_4$.[2] In addition, collision-induced dissociation of the $NiC_4H_8^+$ product[9] shows fragmentation by loss of one or two ethylene neutrals, suggesting the bis(ethylene) structure. Two different, highly specific reaction pathways might explain these results. First, Ni^+ might insert in the central (weakest) CC bond of *n*-butane. Subsequent migration of one β-deuterium atom leads to the intermediate $Ni^+(D)(C_2H_2D_3)$-$(C_2H_2D_2)$. This key intermediate either eliminates $C_2H_2D_4$ or undergoes a second β-deuterium migration, which leads to elimination of D_2. Alternatively, Ni^+ might first insert in a terminal CD bond. Subsequent β-*ethyl* migration to the metal then leads to the same intermediate and the same highly specific products.

Our results indicate that H_2 and C_2H_6 elimination occur on the same time scale, as if both channels share a common rate-limiting step. Either mechanistic alternative would then imply that the measured 400-ns lifetime is that of the $Ni^+(H)(C_2H_5)$-(C_2H_4) intermediate. Accordingly, the insensitivity of the lifetime to collision energy over the range 0.2–5 kcal mol^{-1} seems to rule out initial CC or CH insertion as the rate-limiting step. For if reactants fall into a deep ion-induced-dipole well[10,11] from which CC or CH insertion (k_{ins}) competes with return to reactants (k_{-1}),

we would surely expect the complex lifetime $(k_{ins} + k_{-1})^{-1}$ and probably also the absolute reaction efficiency to be highly sensitive to collision energy. It will be interesting to see whether or not statistical models can explain our new lifetime measurements.

In previous work, CH_4 elimination accounted for 4%–9% of the products at 0.5 eV,[1–3] whereas we observe only 1%. This difference may arise because our reactant energy is unusually low and well controlled. The R2PI process creates the lower energy $^2D_{5/2}$ spin–orbit level of Ni^+ exclusively;[6] our butane is internally cooled to about 100 K by expansion; and the collision energy is well controlled at 0.2 or 5 kcal mol^{-1} by the crossed beam technique. Experiments in other labs have had less sharply defined reactant internal energy, average collision energies of 5–10 kcal mol^{-1}, or both. In addition, room temperature *n*-butane contains several kcal mol^{-1} of internal energy, and the presence of even the first excited spin–orbit level ($^2D_{3/2}$) of the 3d^9 term adds 4.3 kcal mol^{-1} to the reactants. In the usual mechanisms invoking β-transfers to the metal atom, methane elimination cannot occur following central CC insertion or terminal CH insertion. Rather, CH_4 elimination is most easily explained by invoking Ni^+ insertion into a terminal CC bond or into a secondary CH bond followed by subsequent β-hydrogen or β-methyl migration. From the near absence of CH_4 products under our cold reaction conditions, we infer that $Ni^+(^2D_{5/2})$ sees a substantial potential energy barrier along paths leading to terminal CC insertion or secondary CH insertion. To test this inference, we plan to increase the collision energy and to study the reactivity of excited state $Ni^+(^2D_{3/2})$ in the near future. Studies of lifetimes and product branching for Ni^+ complexes with deuterium-labeled *n*-butane could also be revealing.

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