Specific Carbon–Carbon Bond Cleavage in *n*-Pentylbenzene by Bare Nickel(I) in the Gas Phase

Ofer Blum,[†] Patrick O'Bannon,[‡] Detlef Schröder, and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Strasse des 17. Juni 135, Germany

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Summary: When the atomic Ni^+ ion is reacted in the gas phase (Fourier transform ion cyclotron resonance) with n-pentylbenzene, the encounter complex does not decompose via dehydrogenation, which is the usual reaction pattern. The sole process observed corresponds to the specific cleavage of the benzylic carbon–carbon bond followed by loss of C_4H_8. Labeling experiments enable the elucidation of a plausible mechanism of the reaction.

In the gas-phase reactions[1] of "bare" Ni^+ ions with various alkane derivatives, we noted[2] two trends which distinguish the Ni complexes from their Fe^+ and Co^+ congeners: (i) While Fe^+- and Co^+-mediated dehydrogenation is often highly specific, Ni^+ tends to induce hydrogen exchange processes preceding the reductive elimination of molecular hydrogen. (ii) Products due to carbon–carbon bond cleavage are generally more pronounced for the Ni^+ complexes in comparison with the Co^+ and Fe^+ systems. While the electronic origin of these effects remains to be clarified, it is also of interest to recall that some of the Ni^+ systems we studied[3] exhibit a chemistry reminiscent of the gas-phase behavior of Lewis acid complexes. In the present note we describe the chemistry of atomic Ni^+ when it is reacted in the gas phase with *n*-pentylbenzene (1) using Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. To our knowledge, the results are unprecedented in that only one product is observed which corresponds to the exclusive cleavage of the benzylic carbon–carbon bond accompanied by a hydrogen transfer to generate $Ni(C_7H_8)^+$ and C_4H_8. By means of labeling experiments, insight into the possible mechanism of this highly specific reaction is obtained.

Experimental Section

The apparatus (a Spectrospin-CMS-47X equipped with an external ion source) and its operation have been described in detail previously.[3a,4] Atomic Ni^+ is formed via laser desorption/ionization[5] in the external ion source[6] by focusing the beam of a Nd:YAG laser (Spectron Systems, fundamental frequency 1064 nm) onto a high-purity nickel rod which was affixed in the external ion source. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials and lenses. After deceleration, the Ni^+ ions are trapped in the field of the superconducting magnet (Oxford Instruments) which has a maximum field strength of 7.05 T. The metal's most abundant isotope $^{58}Ni^+$ was isolated by using FERETS[7] and allowed to react with the substrate that was present with a constant pressure of (1.8–4.0) × 10^{-8} mbar; reaction times are typically 1–10 s. For collisional cooling of any excited states possibly formed and for removal of kinetic energy remaining from the transfer, argon was present as a buffer gas with a constant pressure of 1.5 × 10^{-7} mbar. The pressures given were measured with an uncalibrated ionization gauge (Balzers IMG 070). When necessary, reaction products were unambiguously identified by exact mass measurements.

Table I. Ni^+-Induced Elimination of $C_4H_{8-x}D_x$ from Deuterated *n*-Pentylbenzenes[a]

precursor	C_4H_8	C_4H_7D	$C_4H_6D_2$	$C_4H_5D_3$
$C_6H_5CD_2(CH_2)_3CH_3$ (**1a**)	100			
$C_6H_5(CH_2)_2CD_2CH_2CH_3$ (**1b**)		61.6	38.4	
$C_6H_5(CH_2)_4CD_3$ (**1c**)			0.9	99.1

[a] Data are given in $\sum C_4H_{8-x}D_x$ = 100%.

The labeled *n*-pentylbenzenes were synthesized and fully characterized using established procedures[8] and purified by preparative gas chromatography.

Results and Discussion

In the reaction of Ni^+ with *n*-pentylbenzene (1), we observe as the only primary product the ion $Ni(C_7H_8)^+$. This corresponds to the loss of C_4H_8 (Δm = 56 amu). As the neutral products of low-energy ion/molecule reactions usually escape experimental detection, several possibilities have to be considered for the nature of Δm = 56 amu: (i) The combined[9] losses of C_4H_6/H_2 or of $2C_2H_4$ are unlikely on thermochemical grounds.[10] They can also be ruled out by analyzing the data obtained for the pentylbenzene isotopomers 1a–1c (Table I). (ii) The formation of cyclobutane is thermochemically feasible, as its heat of formation is only 6.9 kcal/mol higher than that of 1-butene.[10] Nevertheless, the labeling data are not com-

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* To whom correspondence should be addressed.

[†] Present address: Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel.

[‡] Present address: Department of Chemistry, Kenyon College, Gambier, OH.

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(3) (a) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621. (b) Eller, K.; Karrass, S.; Schwarz, H. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1201.

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(7) Forbes, R. A.; Laukien, F. M.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

(8) Wesdemiotis, C.; Schwarz, H.; Van de Sande, C. C.; Van Gaever, F. *Z. Naturforsch.* **1979**, *34B*, 495.

(9) For example, the neutrals do not necessarily correspond to genuine molecules (e.g. C_2H_6 or C_4H_8) but rather to combined losses of small unsaturated species (C_2H_4/H_2; $2C_2H_4$); see: Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 5947 and references therein.

(10) Thermochemical data were taken from: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. ΔH_f(1,3-butadiene) = 26.8 kcal/mol, $\Delta H_f(C_2H_4)$ = 12.5 kcal/mol; ΔH_f(cyclobutane) = 6.8 kcal/mol; ΔH_f(1-butene) = –0.1 kcal/mol.

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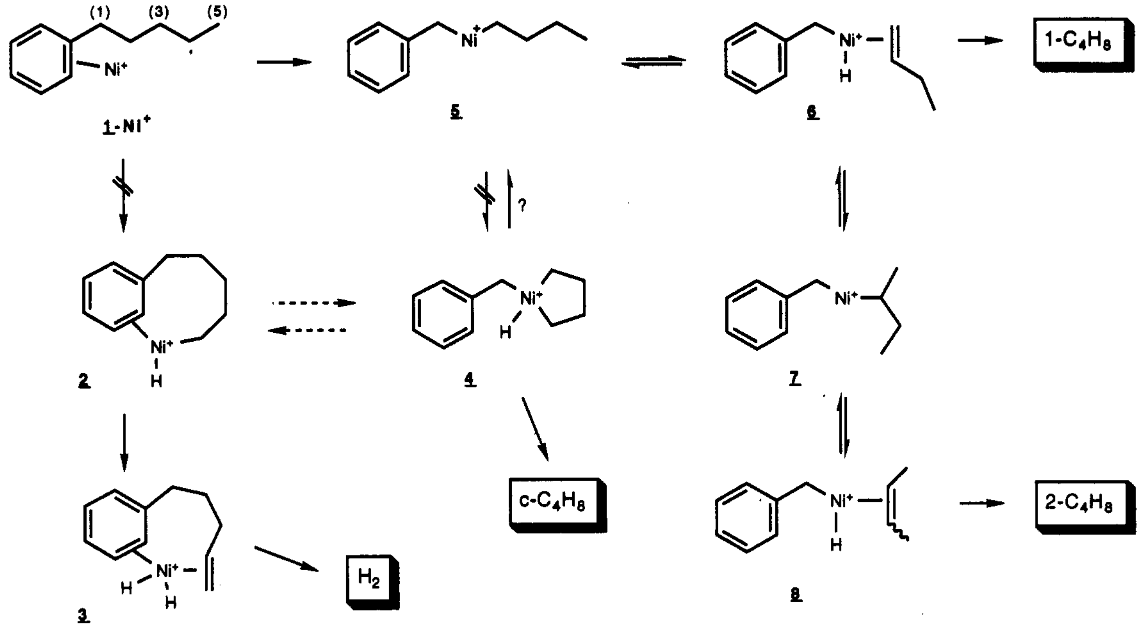
Scheme I



patible with this assignment. (iii) From the analysis of the labeling experiments it follows that the benzylic position of 1 does not contribute at all to the formation of C_4H_8. Further, all three hydrogen atoms of the methyl group are to >99% incorporated in the neutral fragment. The fact that labeling of the internal position (C3) results not only in the exclusive loss of C_4H_7D (61.6%) but also in the elimination of $C_4H_6D_2$ (38.4%) clearly suggests the operation of a hydrogen exchange process.

We have considered several mechanistic scenarios. The simplified mechanism depicted in Scheme I has the merit of being compatible with the experimental findings. We suggest that C_4H_8 loss is *not* initiated by remote functionalization[11] of the terminal C–H group (1-Ni^+ → 2), because 2 is expected to undergo a facile β-hydrogen rearrangement (2 → 3) followed by a reductive elimination of molecular hydrogen. As stated above, no loss of H_2 is observed when Ni^+ is reacted with 1 in the gas phase. Rather, we suggest that the reaction commences with oxidative addition of Ni^+ to the benzylic carbon–carbon bond (1-Ni^+ → 5).[12] This intermediate does not rearrange to the metallacycle 4 (which might be considered to serve as a possible precursor for the reductive elimination of cyclobutane). This conclusion follows immediately from the labeling experiment, as in 4 the originally distinct C2/C5 positions have become structurally equivalent. As a consequence, if 4 would decompose by a C–C reductive elimination, the complex generated from either **1b** and **1c** should exhibit specific loss of $C_4H_6D_2$; this expectation is not borne out experimentally (Table I). It may be suggested that the 5 ⇄ 4 rearrangement occurs but *without* any subsequent *c*-C_4H_8 loss. However, the concomitant structural equilibration between C2 and C5 predicts a >1% loss of $C_4H_6D_2$ from 1c via the 6 ⇄ 7 ⇄ 6 mechanism which we prefer. This is not observed (Table I), and we suggest that 5 undergoes a rapid β-hydrogen transfer (5 → 6). The olefin complex 6 has two basic options: (i) direct olefin detachment; (ii) migratory insertion to isomerize via 7 to 8 from which C_4H_8 can be eliminated. If we ignore the operation of kinetic isotope effects, we arrive at a kinetic scheme according to which the direct loss of C_4H_8 from 6 is ca. 5.5 times faster than the establishment of the equilibria 6 ⇄ 7 ⇄ 8 via the migratory insertion 6 → 7. Actually, if the sequence 6 ⇄ 7 ⇄ 8 is expanded, the mechanism depicted in Scheme I can also explain the minor loss (0.9%) of $C_4H_6D_2$ from 1c.

In conclusion, the encounter complex generated by reacting bare Ni^+ with *n*-pentylbenzene in the gas phase is unique in that no dehydrogenation occurs; rather, the sole process corresponds to the specific activation of the benzylic carbon–carbon bond followed by specific β-hydrogen transfer processes to eventually generate C_4H_8 and $Ni(C_7H_8)^+$.

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[11] For this concept and many examples, see: (a) References 1 and 3b. (b) Schwarz, H. *Acc. Chem. Res.* 1989, *22*, 282. (c) Eller, K.; Schwarz, H. *Chimia* 1989, *43*, 371. (d) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg 1989; p 203.

[12] It is interesting to note that the specific 1,4-dehydrogenation of butane by Ni^+ also commences with insertion of the metal ion in the central CC bond, followed by two consecutive β-hydrogen migrations to generate $Ni(H_2)(C_2H_4)_2^+$: (a) Houriet, R.; Halle, K. F.; Beauchamp, J. L. *Organometallics* 1983, *2*, 1818. (b) Houriet, R.; Halle, L. R.; Houriet, R.; Kappes, M. M.; Staley, R. M.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1982, *104*, 6293. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1983, *105*, 5197. (d) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* 1983, *105*, 736. (e) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; van Koppen, P. A. M.; Bowers, M. T. *J. Am. Chem. Soc.* 1988, *110*, 1.