

Table II. Relative Energy Predictions for Dilithiomethane. The Absolute Energies of the Tetrahedral Singlet are -53.8362 hartrees (SCF) and -54.0216 hartrees (CI)

	E (SCF), kcal	μ (SCF), D	E (CI), kcal	E (CI), ^a kcal
planar singlet	3.2	4.85	7.4	8.3
planar triplet	-15.8	-1.22	+0.9	3.9
tetrahedral singlet	0.0	5.42	0.0	0.0
tetrahedral triplet	-16.6	-0.76	-0.8	+2.1

^a Corrected for unlinked clusters.

tetrahedral triplet. The near degeneracy of these four electronic moieties is to our knowledge without precedent and suggests an urgent need for experimental studies of this simple molecule.

Acknowledgment. We thank Professor Andrew Streitwieser for helpful discussions. This research was supported by the Division of Basic Energy Sciences, through the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory.

References and Notes

- J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 5419 (1976). A semipopular review of this research has been given by T. H. Maugh, *Science*, **194**, 413 (1976).
- P. O. Löwdin, *Adv. Chem. Phys.*, **2**, 207 (1959).
- H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.
- T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry, Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977, pp 1-27.
- R. R. Lucchese and H. F. Schaefer, *J. Am. Chem. Soc.*, **99**, 6765 (1977); B. O. Roos and P. M. Siegbahn, *ibid.*, **99**, 7716 (1977); L. B. Harding and W. A. Goddard, *J. Chem. Phys.*, **67**, 1777 (1977); C. W. Bauschlicher and I. Shavitt, *J. Am. Chem. Soc.*, **100**, 739 (1978).
- B. Roos, *Chem. Phys. Lett.*, **15**, 153 (1972); R. R. Lucchese and H. F. Schaefer, *J. Chem. Phys.*, **68**, 769 (1978).
- E. R. Davidson and D. W. Silver, *Chem. Phys. Lett.*, **22**, 403 (1978).
- R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope, and H. F. Schaefer, *J. Comput. Phys.*, **26**, 243 (1978).

William D. Laidig, Henry F. Schaefer III*

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Received May 8, 1978

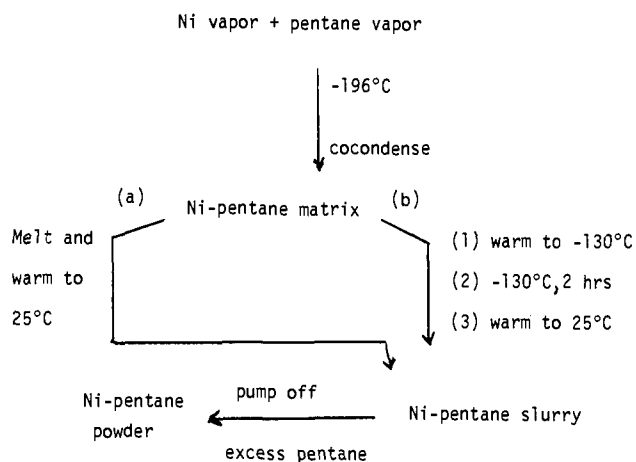
Low Temperature Cleavage of Alkanes by Small Nickel Particles. Clustering of Metal Atoms in Organic Media. 7¹

Sir:

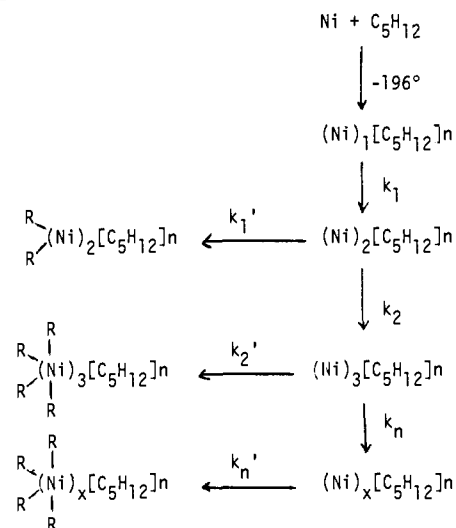
We recently reported chemical and microscopy studies of small metal particles formed by clustering of nickel atoms in organic media.² We have since directed much of our attention to further chemical and catalytic characterization of active metal powders produced by cocondensation of nickel atoms and alkanes, which have been shown to be extremely active and selective hydrogenation catalysts.³ In our previous Ni-alkane work² we had tacitly assumed that the alkanes were simply physis- and chemisorbed on the Ni cluster surfaces, and these intact alkane (hexane) molecules were cleaved upon pyrolysis of the Ni-alkane powders. However, we wish to report here that alkane cleavage (pentane, hexane, or others) occurs at very low temperature, about -130 °C, during formation of Ni clusters from Ni atoms dispersed in the alkane.

When nickel is cocondensed with a high excess of pentane at -196 °C and the resultant matrix allowed to warm to room temperature, a fine black powder is obtained after vacuum removal of excess pentane (Scheme Ia). This stable black powder contains a remarkably large amount of organic material. Elemental analyses, pyrolyses, and exhaustive high

Scheme I



Scheme II



temperature H_2 and O_2 treatments have all independently been in experimental agreement, and have revealed a Ni:C:H mole ratio of 2-5:1:2 depending upon preparative details. When a large excess of pentane is used (>300 -fold) during the cocondensation, the final dry powder is nonferromagnetic with very small nickel crystallites. If a lesser amount of pentane is used (<100 -fold), larger ferromagnetic particles are obtained. It is interesting that the larger ferromagnetic particles contain less organic material than the nonferromagnetic particles (5:1:2 vs. 2:1:2 Ni:C:H ratios, respectively). Furthermore, we have found that by allowing the Ni-pentane matrix to warm to -130 °C (pentane slush) and remain at that temperature for 2 h, followed by normal warm-up to room temperature, nonferromagnetic powder can be obtained with as little as a 40-fold excess of pentane (Scheme Ib). This powder then possesses the Ni:C:H ratio similar to the powder prepared by using a large pentane excess (>300 -fold), and powder X-ray studies yield crystallite size estimates for both of these nonferromagnetic samples as <30 Å, whereas the ferromagnetic samples consistently show >80 -Å crystallite sizes. (These data show, of course, only the larger crystallites present, which are probably a fairly small percent of the total Ni, much of it surely being essentially noncrystalline.) These results strongly suggest the presence of a competition between nickel particle growth in pentane (k) and nickel particle reaction with pentane (k'). Scheme II illustrates this competition in general form. Thus, we believe nickel clusters form at very low temperatures, and these grow larger with temperature increase (-196 to -130 °C). However, also with temperature rise, rates of oxidative

Table I. Products Evolved during Hydrogenation and Hydrolysis of a Nonferromagnetic Ni-Pentane Powder (Ni:C:H, ~2:1:2)

temp, °C	products, mol % ^a					
	CH ₄	CO ₂ ^c	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
25			H ₂ ^b			
		1.8	0.9	3.6	5.4	8.0
300	10	38	22	7.4	2.5	1.5
			H ₂ O ^d			
75	<i>e</i>	9.0	2.2	17	23	48

^a Overall percent for 25 and 300 °C treatments. ^b 150 Torr of H₂, 30 h, 25 °C; 60 Torr of H₂, 6 h, 300 °C; 150 mg of Ni-pentane. ^c Variable, dependent upon airless care during workup. ^d 2-mL H₂O reflux with 300 mg of Ni-pentane for 1 h. ^e Not measured but non-condensable gas observed.

addition and/or abstraction processes with (Ni)_n and C₅H₁₂ increase and become more and more competitive, and, when stable molecular structures are forced to be attained by warming to room temperature, the final Ni-organic composition depends on the experimental warm-up rate. Currently we doubt that nickel atoms are actually reacting with pentane for several reasons: (1) metal atoms including Ni are known to form clusters readily in inert matrices even as low as 10 K;^{4,5} (2) we can visually observe the formation of Ni particles in the -196 to -130 °C range and feel certain that no Ni atoms exist at 130 °C (pentane liquid), the temperature where pentane reaction is obviously occurring at a very competitive rate; and (3) the only data yet reported on metal atom-alkane codepositions⁶ indicate that V atom-alkane reactions are not occurring at the temperature where V clustering is taking place.

What is the form of the organic material in the "pseudo Ni-organometallic"? This question becomes exceedingly important for two reasons: (1) learning the structure of the R group attached to the nickel clusters should teach us a great deal about how the low temperature reactions occur, and (2) the presence of more organics allows the preparation of smaller crystallite nonferromagnetic nickel particles that are more stable to sintering and more active in some catalytic processes than the larger particle (less organics) ferromagnetic samples (nonferro, 260-280 °C with gross sintering; ferro, 220-240 °C).³ These results indicate that the carbonaceous species stabilize the nearly amorphous nickel framework.

ESCA studies incorporating first surface analysis of "as is" samples followed by sputtering to several different depths and then further analyses have demonstrated that the carbon is homogeneously dispersed throughout the nickel, and that the carbon is *not in the form of carbides* but rather more likely sp²- and sp³-bound carbon species. Addition of H₂ or H₂O to the Ni-pentane powder yields distributions of evolved organics that are very similar, identified as CH₄, C₂H₆, C₃H₈, C₄H₁₀, and C₅H₁₂ (cf. Table I). No organics containing more than five carbons were found. The similarity of product distributions for hydrogenation and hydrolysis and the mild conditions employed strongly suggest that the pentane cleavage reactions are not occurring during the workup, but occurred during the Ni-pentane codeposition—warm-up procedure as previously discussed.

These results clearly demonstrate cleavage of pentane by nickel clusters at very low temperatures and retention of organic fragments to produce thermally stable catalytically active "organometallic" powders. The Ni-Ni framework is stabilized toward sintering by strongly bound fragments of the alkane, which apparently are present as alkyl radical and carbenoid-like species.

Acknowledgments. Support of the National Science Foundation (CHE-7402713) is gratefully acknowledged. Also,

helpful discussions and ESCA work by Curt White and Charles Kibby of the Pittsburgh Energy Research Center are greatly appreciated.

References and Notes

- (1) Part 6 of this series: K. J. Klabunde, D. Ralston, R. Zoellner, H. Hattori, and Y. Tanaka, *J. Catal.*, in press.
- (2) K. J. Klabunde, H. F. Efner, T. O. Murdock, and R. Ropple, *J. Am. Chem. Soc.*, **98**, 1021 (1976).
- (3) K. J. Klabunde, S. C. Davis, H. Hattori, and Y. Tanaka, *J. Catal.*, in press.
- (4) M. Moskovits and G. A. Ozin, Ed., "Cryochemistry", Wiley-Interscience, New York, N.Y., 1976, p 395.
- (5) M. Moskovits and J. Hulse, *Surf. Sci.*, **57**, 125 (1976).
- (6) W. E. Klotzbucher, S. A. Mitchell, and G. A. Ozin, *Inorg. Chem.*, **16**, 3063 (1977).

Stephen C. Davis, Kenneth J. Klabunde*

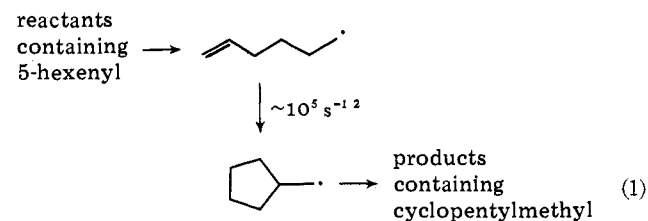
Department of Chemistry, University of North Dakota
Grand Forks, North Dakota 58202

Received May 9, 1978

Intramolecular 1,4 Proton Transfer in the 5-Hexenyl Anion. The 5-Hexenyl Probe as a Detector of Both Alkyl Radical and Anion Intermediates

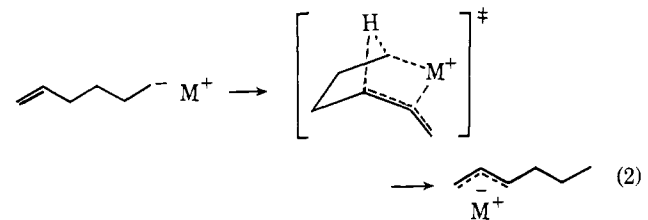
Sir:

The cyclization of 5-hexenyl to cyclopentylmethyl radicals (eq 1) is a valuable probe for alkyl radical reaction interme-



diates.¹ Because the corresponding cyclization of 5-hexenyl anions often occurs to a negligible or limited extent, this probe is especially useful when *both* alkyl radicals and anions may be intermediates.

During one such application, we obtained unexpected products that point to isomerization of the 5-hexenyl anion by an intramolecular 1,4 proton transfer (eq 2). While this ra-



tional but unprecedented reaction complicates slightly the interpretation of results, it also extends the usefulness of the probe. Under favorable circumstances, the 5-hexenyl probe detects both radical and anion intermediates separately and specifically.

The expected products of reactions of 5-hexenyl chloride in ethers with alkali metals were 1-hexene and methylcyclopentane. In addition, there were formed 2-hexenes and dimers **1** and **2**. As anticipated, the normal Wurtz coupling product, 1,11-dodecadiene, was not formed in significant amounts.³

