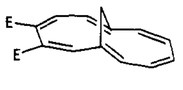
Table I. Physical and Spectroscopic Properties of Cycloadduct 3 and Homoheptalene Diester 5

3 (mp 120 °C dec)
^{1}H NMR (CDCl$_3$) δ 7.08 (d, 1, *J* = 10 Hz), 6.58–5.98 (m, 5), 5.71 (dd, 1, *J* = 10, 4 Hz), 4.30 (d, 1, *J* = 4 Hz), 3.07 (d, 1, *J* = 12 Hz), 2.67 (d, 1, *J* = 12 Hz)
^{13}C NMR (CD$_3$COCD$_3$) δ 136.8 (d), 132.9 (s), 130.1 (d), 129.2 (d), 126.8 (d), 126.7 (d), 125.1 (d), 115.3 (d), 110.5 (s), 109.9 (s), 108.6 (s), 108.1 (s), 52.3 (d), 49.2 (s), 46.0 (s), 38.1 (s), 30.3 (t)
IR (KBr) 2995, 2915, 2890, 2215, 1447, 1333, 1277 (s), 1075 (s), 930 (vs), 886 (vs), 767 (vs), 730 (vs), 717 (vs) cm^{-1}
UV (CH$_3$CN) λ_{max} 230, 298

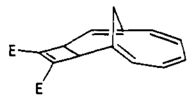
5 (mp 139 °C)
^{1}H NMR (CDCl$_3$) δ 7.19 (s, 1), 7.00 (d, 1, *J* = 4 Hz), 6.13 (m, 2), 5.93 (d, 1, *J* = 4 Hz), 5.64 (m, 3), 5.10 (d, 1, *J* = 12 Hz), 4.95 (d, 1, *J* = 12 Hz), 3.72 (s, 3), 3.69 (s, 3)
^{13}C NMR (CDCl$_3$) δ 168.4 (s), 167.6 (s), 145.2 (s), 144.3 (d), 144.1 (d), 143.9 (s), 137.2 (d), 136.0 (d), 130.5 (d), 130.4 (s), 130.3 (s), 129.5 (d), 129.3 (d), 126.0 (d), 52.2 (q), 52.1 (q), 31.7 (t)
IR (KBr) 2975, 2920, 1708 (s), 1685 (s), 1585, 1417, 1225 (s), 1055, 915, 772 cm^{-1}
UV (CH$_3$CN) λ_{max} 226 sh, 270, 413

philic attack on other bridged annulenes.[8]

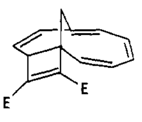
DMAD adds much more slowly than TCNE to homoazulene. At 82 °C, however, (refluxing ClCH$_2$CH$_2$Cl, 36 h) the reaction proceeds smoothly to give the homoheptalene diester **5** in 91% yield, presumably via the [2 + 2] cycloadduct **6**. The spectroscopic properties of this blood-red product (see Table I) support the assigned structure. Of special interest are the low-field ^{1}H NMR signals for the CH$_2$ bridge in **5** (δ ca. 5.0), which reflect a paramagnetic ring current[9] in the newly created [4*n*]annulene perimeter and contrast sharply with those for the CH$_2$ bridge in homoazulene (δ ca. −1.0). ^{1}H NMR spectroscopy rules out an α,β-disubstituted homoheptalene derived from the expected [2 + 2] cycloadduct **7**. The addition of DMAD probably follows a stepwise course via an intermediate analogous to **4**, but the zwitterion cyclizes to form **6** rather than **7** for reasons that are presently not clear.



5



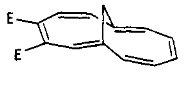
6



7

E = COOCH$_3$

Structure **5** accounts well for the small coupling constant (*J* = 4.1 Hz) associated with the clean olefinic AB quartet in the ^{1}H NMR spectrum of this homoheptalene derivative.[10] A significantly larger coupling constant would be expected for the alternative Kekulé structure (**8**) or the fully delocalized structure (**9**).[10] The appearance of an NMR singlet (δ 7.19) and a doublet (δ 7.00) at abnormally low field further strengthens the conclusion that this molecule exists predominantly, if not exclusively, in the bond-localized form **5**.[11]



8

9

Vogel and co-workers have previously prepared the unsubstituted homoheptalene molecule by an elegant ten-step synthetic sequence.[12] The parent hydrocarbon exhibits an even more pronounced paramagnetic ring current (^{1}H NMR) and is likewise characterized by double-bond localization in the ground state (^{13}C NMR and X-ray).[12,13] Equilibration between the two isoenergetic (enantiomeric) Kekulé structures in this case was found to occur with $\Delta G^{\ddagger}$ = 5 kcal/mol.[12]

By the rules of orbital symmetry conservation,[14] disrotatory electrocyclic opening of the cyclobutene ring in **6** to give **5** constitutes a forbidden ground-state reaction. Most likely, therefore, the isomerization passes through a symmetry-allowed ten-electron pericyclic transition state, producing **8** as the initial product, which then rearranges by a low-energy bond-switching process to the thermodynamically more stable isomer **5**. Completely analogous periselectivity has been observed in the disrotatory opening of bicyclo[4.2.0]octa-2,4,7-triene derivatives to give substituted cyclooctatetraenes.[15]

In conclusion, we emphasize the similarity between the [2 + 2] cycloaddition reactions of homoazulene and the known reactions of azulene with electron-deficient cycloaddends. Our results represent the first *chemical* evidence to support the conclusion (previously drawn from spectroscopic data) that the electronic properties of homoazulene resemble those of the prototypical nonalternant hydrocarbon azulene. As a bonus, the DMAD cycloaddition provides a novel high-yield route to the 4*n* π-electron homoheptalene ring system, which should also be weakly nonalternant through homoconjugation; more thorough studies of homoheptalenes will now be possible.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health (CA 23488), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Registry No. 1, 65754-71-4; **3**, 81741-07-3; **5**, 40985-77-1; TCNE, 670-54-2; DMAD, 762-42-5.

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(8) Takahashi, K.; Takase, K.; Kagawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 1186 and references cited therein.

(9) (a) Longuet-Higgins, H. C. Special Pub.—*Chem. Soc. No. 21*, **1967**, 109. (b) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 4811.

(10) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon: New York, 1969; Chapter 4.

(11) See ref 10, Chapter 3-3.

(12) Vogel, E.; Königshofen, H.; Müllen, K.; Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 281.

(13) Mugnoli, A.; Simonetta, M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 822.

(14) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970.

(15) Paquette, L. A.; Gardlik, J. M.; Johnson, L. K.; McCullough, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 5026 and previous papers in this series.

Reactions of Aliphatic Radicals with Benzylaquocobaloxime: Kinetics of Coupling Reactions As Studied by Novel Kinetic Competition Methods

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Organocobaloximes[1] are good candidates to employ in a search for the rarely encountered bimolecular homolytic displacement reactions, because the leaving group is the stable cobalt(II) cobaloxime. Catalytic reactions of selected organocobaloximes with tetrahalomethanes[2] and arenesulfonyl chlorides[3] are characterized by products and other features that suggest that one step is a reaction between the cobaloxime and ·CX$_3$ or ArSO$_2$·, respectively,

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(1) Cobaloxime is the trivial name given to bis(dimethylglyoximato)cobalt complexes [Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97], designated Co(dmgH)$_2$, where dmgH$^-$ is the monoanion of dimethylglyoxime (2,3-butanedione dioxime).

(2) (a) Gupta, B. D.; Funabiki, T.; Johnson, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 6697. (b) Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1978**, 1821. (c) Gupta, B. D.; Funabiki, T.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1977**, 653; (d) Bougeard, P.; Gupta, B. D.; Johnson, M. D. *J. Organomet. Chem.* **1981**, *206*, 211.

(3) (a) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013. (b) Cooksey, C. J.; Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Bialkowska, E.; Duong, K. N. V.; Gaudemer, A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2611.

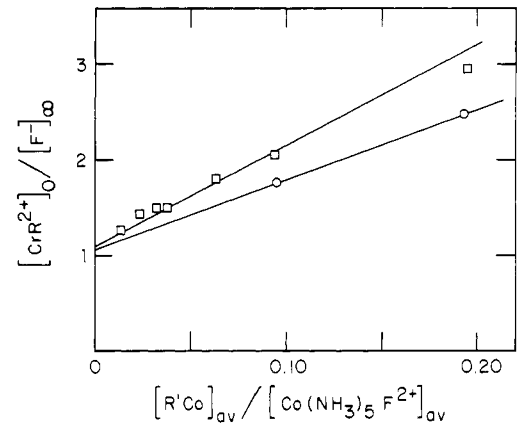

Figure 1. Analysis of data for kinetic competition of $\cdot CH(CH_3)OC_2H_5$ for reaction with $PhCH_2Co(dmgH)_2OH_2$ (eq 2) and $Co(NH_3)_5F^{2+}$. Data are plotted according to eq 7 ($[H^+]$: 1.00 M (□); 0.150 M (○)).

possibly by homolytic displacement.

We have now shown that aliphatic radicals ($R\cdot$) react similarly. Alkyl- ($R'Co(dmgH)_2OH_2$) and benzylcobaloximes yield RR′ and $PhCH_2R$, respectively. The processes were confirmed to be bimolecular reactions and their rate constants determined with new methods of chemical competition. Reactions of benzylaquocobaloxime in aqueous perchloric acid with the radicals $\cdot CH(CH_3)OC_2H_5$ and $\cdot C(CH_3)_2OH$ are considered here.

The complex $(H_2O)_5CrCH(CH_3)OC_2H_5^{2+}$[4] undergoes reversible homolytic dissociation (eq 1).[5] If benzylaquocobaloxime

$$CrCH(CH_3)OC_2H_5^{2+} \rightleftarrows Cr^{2+} + \cdot CH(CH_3)OC_2H_5 \quad (1)$$

$$PhCH_2Co(dmgH)_2OH_2 + \cdot CH(CH_3)OC_2H_5 \rightarrow A + Co(dmgH)_2OH_2 \quad (2)$$

$$Co(dmgH)_2 + 2H^+ \rightarrow Co^{2+} + 2H_2dmg \quad (3)$$

is added, the sole organic product is $PhCH_2CH(CH_3)OC_2H_5$ (A) (eq 2). The cobalt(II) complex is converted to Co^{2+} very rapidly (eq 3).[6]

Similarly, homolysis of $(H_2O)_5CrC(CH_3)_2OH^{2+}$ forms the 2-hydroxy-2-propyl radical (eq 4),[5] which subsequently forms

$$CrC(CH_3)_2OH^{2+} \rightleftarrows Cr^{2+} + \cdot C(CH_3)_2OH \quad (4)$$

$$PhCH_2Co(dmgH)_2OH_2 + \cdot C(CH_3)_2OH \rightarrow B + Co(dmgH)_2OH_2 \quad (5)$$

$$CrC(CH_3)_2OH^{2+} + \cdot C(CH_3)_2OH \rightarrow HOC(CH_3)_2C(CH_3)_2OH + Cr^{2+} \quad (6)$$

1-phenyl-2-methyl-2-propanol (B) (eq 5) and smaller amounts of pinacol (eq 6).[7] Alternatively, homolysis[8] of $(H_2O)_5CrCH_2Ph^{2+}$ in the presence of H_2O_2, $PhCH_2Co(dmgH)_2OH_2$, and 2-propanol (0.1–0.5 M)[9] can be used for eq 5.[10,11]

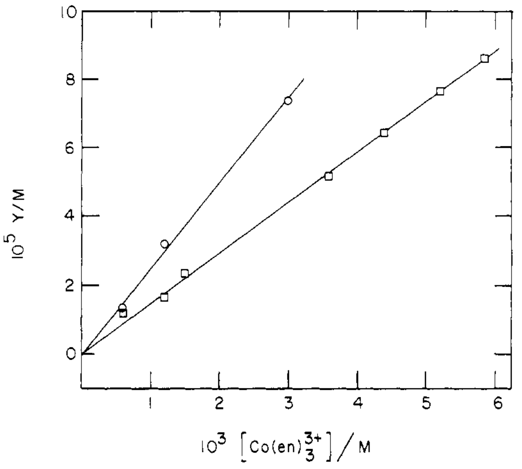

Figure 2. Analysis of the data for kinetic competition of $\cdot C(CH_3)_2OH$ for reaction with $PhCH_2Co(dmgH)_2OH_2$ (eq 5) and $Co(en)_3^{3+}$. Data are plotted according to eq 8 ($[H^+]$: 1.00 M (□); 0.100 M (○)). The values of $\Delta[Co(en)_3^{3+}]$ required for the calculation of Y are taken as the difference in $\Delta[R'Co]$ in the absence of $Co(en)_3^{3+}$ and that found in its presence.

Competition experiments were designed to study the kinetics of reactions 2 and 5. In the former case the competing reagent was $Co(NH_3)_5F^{2+}$, which prevents side reactions by oxidizing the Cr^{2+} rapidly, while competing at a known rate, k_F.[12-14] The competition experiments for eq 5 consisted in using a mixture of $CrCH_2Ph^{2+}$, H_2O_2, 2-propanol, $PhCH_2Co(dmgH)_2OH_2$, and $Co(en)_3^{3+}$; again, the basis of the method is the known reaction rate between $Co(en)_3^{3+}$ and $\cdot C(CH_3)_2OH$.[15] The mechanisms shown lead to the following equations for the respective cases:

$$\frac{[CrR^{2+}]_0}{[F^-]_\infty} = \frac{[CrR^{2+}]_0}{[CrR^{2+}]_0 - \Delta[R'Co]} = 1 + \frac{k_2}{k_F}\frac{[R'Co]_{av}}{[Co(NH_3)_5F^{2+}]_{av}} \quad (7)$$

$$Y = \frac{\Delta[Co(en)_3^{3+}]}{\ln\{[R'Co]_0/([R'Co]_0 - \Delta[R'Co])\}} = \frac{k_{en}}{k_5}[Co(en)_3^{3+}]_0 \quad (8)$$

Graphical analysis (Figures 1 and 2) leads to the values $k_2 = (1.72 \pm 0.13) \times 10^7$ and $k_5 = 1.2 \times 10^7$ M^{-1} s^{-1} at 25.0 °C and 1.0 M H^+. Data at other $[H^+]$ required allowance for the protonation of the organocobaloxime.[16] With the assumption that both species react with $\cdot CH(CH_3)OC_2H_5$ (the acidic and basic forms of the cobaloxime having respective rate constants desig-

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[4] Schmidt, W. O.; Swinehart, J. H.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 1117.

[5] Kirker, G. W.; Espenson, J. H.; Bakač, A. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

[6] The Co(II) complex $Co(dmgH)_2OH_2$ is unstable in acidic solution, reacting very rapidly to form Co^{2+}(aq) and free $dmgH_2$: Adin, A.; Espenson, J. H. *Inorg. Chem.* **1972**, *11*, 686. Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435.

[7] It is presumed that pinacol is formed by the analogous reaction of the organochromium ion (eq 6). The self-reaction between a pair of $\cdot C(CH_3)_2OH$ radicals results only in disproportionation. Detection of its dimer, pinacol, requires a different reaction pathway such as eq 6.

[8] Nohr, R. S.; Espenson, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 3392.

[9] Unlike $CrCH(CH_3)OC_2H_5^{2+}$, the complex $CrC(CH_3)_2OH^{2+}$ cannot be purified by ion exchange due to its short lifetime in solution.[5] For the same reason the handling of solutions of the latter becomes difficult. The method utilizing the slowly homolyzing benzylchromium has the further advantages that this complex can be purified by ion exchange and its solutions handled easily.

[10] The Cr^{2+} formed from $CrCH_2Ph^{2+}$ reacts with H_2O_2 to generate $HO\cdot$, which in turn reacts with the alcohol to form the desired radical [Farhataziz; Ross, A. B. "Selected Specific Rates of Reactions of Transients from Water in Aqueous Solutions. III. Hydroxyl Radical and Perhydroxyl Radical and Their Radical Ions"; National Bureau of Standards Report No. NRSDS-NBS-59, 1977].

[11] In this system the radical does not undergo any side reactions, and B is the only product formed. Because $PhCH_2\cdot$ is completely unreactive with the other species present, it produces only bibenzyl by dimerization; in contrast, no bibenzyl is formed if H_2O_2 is omitted. The same mixture lacking the cobaloxime produces no B, eliminating from consideration the reaction $CrCH_2Ph^{2+} + \cdot C(CH_3)_2OH \rightarrow B + Cr^{2+}$.

[12] The rate constant is $k_F = 1.2 \times 10^6$ M^{-1} s^{-1} at 25.0 °C, $\mu = 1.0$ M, determined based on competition with the known reaction[13] with $Co(NH_3)_5Cl^{2+}$.

[13] Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1977**, 1056.

[14] The experiments had $[Co(NH_3)_5F^{2+}]_0 > [R'Co]_0 > [CrR^{2+}]_0$. This takes $[Co(NH_3)_5F^{2+}]$ and [R′Co] each sufficiently constant as to be approximated by an average value, which is correct to within 15%. The extent of reaction was determined spectrophotometrically, by measuring the change in cobaloxime concentration.

[15] The rate constant at pH 0–3 is $k_{en} = 1.7 \times 10^5$ M^{-1} s^{-1}: Shimura, M.; Espenson, J. H.; Bakač, A. *Inorg. Chem.*, in press.

[16] The value $K_H = 2.6 \pm 0.3$ M^{-1} for the equilibrium $PhCH_2Co(dmgH)_2OH_2 + H^+ \rightleftarrows PhCH_2Co(dmg_2H_3)OH_2^+$ was determined in solutions containing 1.0 M 2-propanol; it is within experimental error of the value 2.4 M^{-1} found in water by Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1973**, *95*, 3166.

nated k_{2A} and k_{2B}), the data yield the following rate constants (M^{-1} s^{-1}) at 25.0 °C: $k_{2A} = (1.9 \pm 0.1) \times 10^7$; $k_{2B} = (5.9 \pm 0.7) \times 10^6$; $k_{5A} = (1.28 \pm 0.06) \times 10^7$; $k_{5B} = (5.2 \pm 0.2) \times 10^6$. The minor differences between acidic and basic forms are not unexpected; protonation occurs at a site far removed from the reaction center and produces a small effect in the direction expected from inductive effects.[17]

Reactions typified by eq 2 and 5 appear quite general for aliphatic radicals (except benzyl), and most organocobaloximes (except aryls) react similarly. Although the phrase homolytic displacement has been used, it is recognized that a mechanism consisting of radical addition and reductive elimination also agrees with the results. Further kinetic and stereochemical studies are in progress.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract No. W-7405-ENG-82.

Registry No. $PhCH_2Co(dmgH)_2OH_2$, 38721-38-9; $\cdot C(CH_3)_2OH$, 5131-95-3; $\cdot CH(CH_3)OC_2H_5$, 2229-06-3.

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(17) Effects of a similar magnitude were noted in the reaction of Cr^{2+} with benzylaquocobaloxime, a process that also proceeds by the S_H2 mechanism, for which k_A and k_B are 7.3 and 5.0 M^{-1} s^{-1}, respectively [Espenson, J. H.; Shveima, J. S. *J. Am. Chem. Soc.* **1973**, *95*, 4468].

Chemistry of Cyclic Olefins and Polyenes on Nickel and Platinum Surfaces

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Acyclic olefins and alkynes chemisorb on clean metal surfaces in a largely irreversible fashion because of the facility with which C–H bond breaking occurs from thermally excited states derived from the initial, π-bound chemisorption states. In contrast, cyclohexene and the cyclohexadiene isomers undergo dehydrogenation on clean Ni and Pt surfaces at 0–130 °C to form chemisorbed benzene.[1] Facile dehydrogenation of chemisorbed cyclic olefins is expected because some of the hydrogen atoms bonded to saturated carbon centers will closely approach the metal surface.[2] Accordingly, we projected a dehydrogenation process general to cyclic olefins on clean, atomically flat metal surfaces (1) whereby a delocalized $c\text{-}C_nH_n$ state might be generated at

$$M\text{-}(c\text{-}C_nH_m) \rightarrow M\text{-}(c\text{-}C_nH_n) + M\text{-}H \qquad (1)$$

moderate temperatures. We describe here an ultra high vacuum study[3,4] of C_4–C_8 cyclic olefin and polyene chemisorption on Ni and Pt surfaces. A mechanistic definition for the novel surface mediated conversions of cycloheptatriene and norbornadiene to benzene is also presented.

If the postulated (eq 1) dehydrogenation process prevails, then even-membered rings would produce species *potentially* displaceable as C_nH_n molecules. In fact, cyclobutene chemisorbed irreversibly on Ni and Pt; no hydrocarbon species could be either desorbed thermally or displaced by $P(CH_3)_3$. As noted above, cyclohexene and cyclohexadiene are converted to benzene on all Ni and Pt surfaces.[1] Cyclooctene and 1,5-cyclooctadiene were partially converted to chemisorbed cyclooctatetraene on Pt(111) as established by $P(CH_3)_3$ displacement reactions. Thus, sequence 1 appears to be a common but not necessarily *dominant* one for cyclic olefins with $n(C_n)$ an even number on these[3] surfaces. Only for $n(C_n) = 6$ is sequence 1 the dominant one *established*[1,5] for the surfaces[3] investigated.

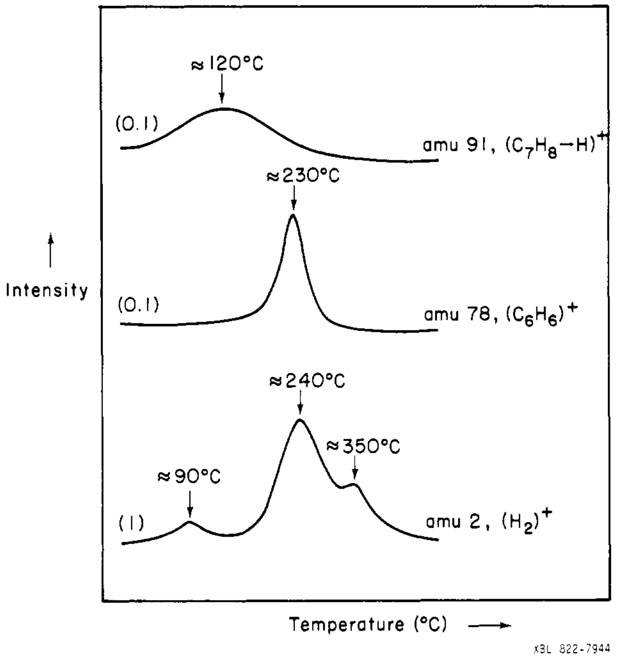

Figure 1. In the rapid heating (20 °C s^{-1}) of Ni(100)–cycloheptatriene, three different species desorbed from this surface: cycloheptatriene, hydrogen, and benzene; these competing thermal processes of reversible cycloheptatriene desorption, decomposition, and benzene formation, respectively, are illustrated with the intensities of the major ions of 91, 2, and 78 plotted as a function of temperature. For normalization of intensities, the parenthetical numbers should be used. The (0.1) value simply indicates that the intensities relative to the (1.0) set should be decreased by a tenth for direct comparisons of intensities of all three molecular species. The low-temperature H_2 desorption maximum observed for Ni(100)–cycloheptatriene coincides with that for Ni(100)–H at comparable H atom coverages—presumably this hydrogen is formed from hydrogen atoms generated in the $C_7H_8 \rightarrow C_7H_7$ process. The two high-temperature H_2 desorption maxima observed for this system and also for Pt(111)–norbornadiene (Figure 2) show that the gross decomposition of the major hydrocarbon fragments is a multistepped process; however, no mechanistic interpretation is warranted based on available data.

For the odd-membered cyclic olefins, sequence 1 would produce a bound C_nH_n "radical" that would not be thermally desorbable or chemically displaceable as a C_nH_n radical. Cyclopentene chemisorption was irreversible on Pt(111) as expected (eq 1),[6]

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(1) Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 0000.

(2) (a) Such a stereochemistry in the initial chemisorption state invariably leads to carbon–hydrogen bond breaking on metal surfaces.[1,2b] (b) Muetterties, E. L. *ACS Symp. Ser.* **1981**, *155*, 273.

(3) The metal surfaces studied were Ni(111), Ni(100), Ni(110), Pt(111), Pt 6(111) × (111), and Pt(100) for $n(C_n) = 6$ and Ni(100), Pt(111), and Pt(100) for the others.

(4) (a) The general experimental procedure for these ultra high vacuum studies, the metal surface cleaning protocols, and the Auger spectroscopic and calibration techniques have been described earlier.[1,4b–d] (b) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 773. (c) Friend, C. M.; Stein, J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767. (d) Friend, C. M.; Gavin, R. M.; Muetterties, E. L.; Tsai M.-C. *J. Am. Chem. Soc.* **1980**, *102*, 1717.

(5) Reaction sequence 1 may be more general and more dominant than it appears from our thermal desorption and chemical displacement reactions; spectroscopic studies, now in progress, are required to pursue this possibility. A problem in characterization of the reaction 1 hypothesis by desorption or displacement studies is that the binding of a C_nH_n species to a specific metal surface may be too strong for facile displacement and thermal reactivity may be too high to allow characterization by thermal desorption. In the decomposition of cyclobutene on the Pt(111) and Pt(100) surfaces, there were two H_2 desorption maxima of relative intensities of ~2 and 4 with lower temperature maxima at 135 and 100 °C, respectively. These data are consistent with, but do not define, the process

$$Pt\text{-}c\text{-}C_4H_6 \xrightarrow{<100\text{-}135\ °C} Pt\text{-}c\text{-}C_4H_4 + Pt\text{-}H$$

(6) Presumably, cyclopentene generates $\pi\text{-}C_5H_5$ states but our spectroscopic studies of this system are presently incomplete.