gesting that it represents one quantum of the a_{1g} C$\equiv$N stretching vibration (ground-state value = 2141 cm^{-1})[10] built upon the 34,360-cm^{-1} origin of ${}^1A_{1g} \rightarrow aA_{2u}$. Band IV is logically attributed to a CT transition to a spin-orbit mixed E_u (${}^3E_u$, ${}^3B_{1u}$, ${}^3A_{2u}$, ${}^1E_u$) state. Again, our interpretation is in basic agreement with the MCD spectral placement[3] of a doubly degenerate state near 35 kcm^{-1}.

The band shapes generally substantiate the interpretation put forward above and give further insight into the nature of the CT and LF excited states of $Ni(CN)_4{}^{2-}$. Transitions to the $a_{2u}(4p_z,\pi^*CN)$ orbital should slightly strengthen the Ni—C bonds, while weakening the C$\equiv$N ones. Excited states derived from the d $\rightarrow$ a_{2u} transitions should be rigorously planar and not differ significantly in equilibrium internuclear positioning from the ground state, if anything experiencing somewhat reduced Ni–C bond lengths. The fact that the CT transitions give rise to sharp bands, therefore, is in full accord with theory. Of the two LF bands which can be clearly observed, I is unusually broad, as expected from the earlier considerations of the highly distorted nature of the ${}^1B_2$ excited state.[7]

Our analysis of the electronic spectrum of $Ni(CN)_4{}^{2-}$ has emphasized the importance of having both low-temperature polarized absorption and MCD spectral data available for assignment purposes. It is highly encouraging that both sets of data fit together as well as they do, providing a consistent interpretation of the main features of the $Ni(CN)_4{}^{2-}$ spectrum. We will use this interpretation as the foundation for discussion of the liquid helium polarized spectra of $Pt(CN)_4{}^{2-}$ in a subsequent paper.

Acknowledgment. Research at the California Institute of Technology was supported by the Army Research Office—Durham.

---

[10] D. Jones, I. J. Hyams, and E. R. Lippincott, *Spectrochim. Acta, Part A*, **24**, 973 (1968).

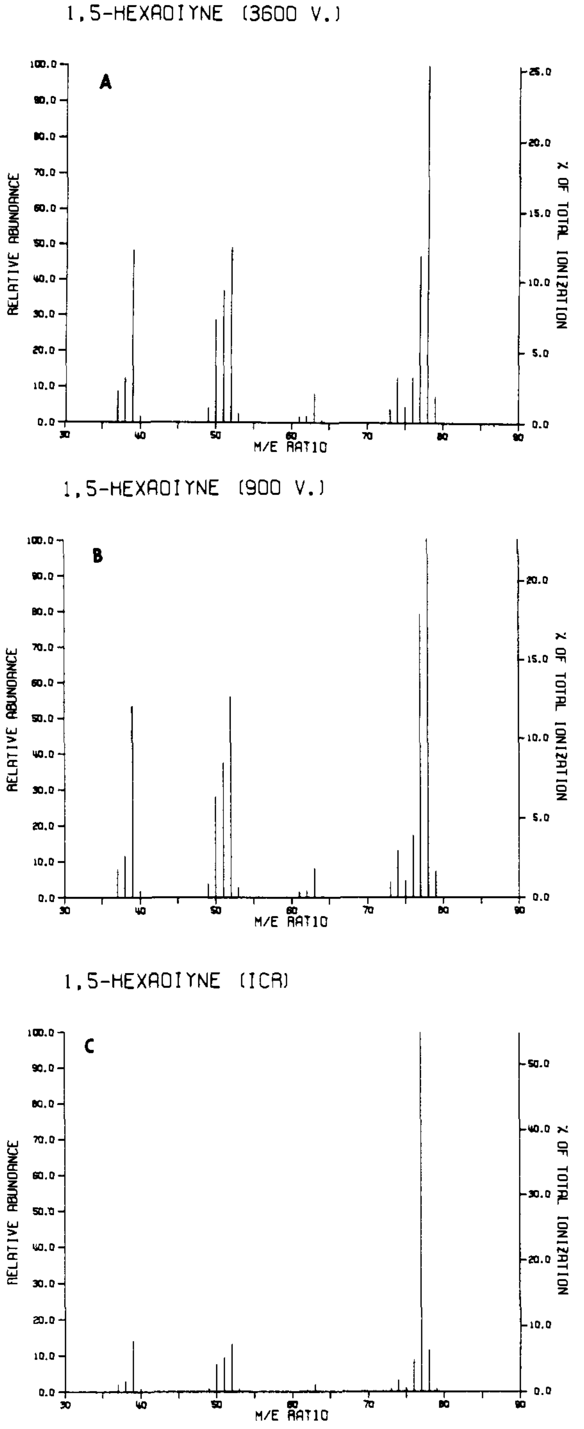
*Address correspondence to this author at the California Institute of Technology.

Charles D. Cowman, C. J. Ballhausen, Harry B. Gray*
Contribution No. 4197
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91109
Chemical Laboratory IV, H. C. Orsted Institute
Universitetsparken 5, 2100 Copenhagen, Denmark
Received July 11, 1973

The Unusual Loss of Hydrogen from Ionized 1,5-Hexadiyne

Sir:

Most mass spectral fragmentations occur in times less than 10^{-5}–10^{-6} sec. Thus, mass spectra do not show extensive variations from instrument to instrument, and accurate energetic data can often be obtained with conventional source designs. Unfortunately, access to the time region of prime importance (*i.e.*, less than 10^{-6} sec) can only be gained by special techniques such as field ionization[1] or distinctive apparatus for metastable ion studies.[2] Of considerable interest would be the discovery of a compound which undergoes significant fragmentation in times equal to or *greater* than 10^{-5} sec. Here we wish to report such a compound which undergoes a very slow loss of H. Indeed, this material, 1,5-hexadiyne, is isomeric with benzene, and our results may pertain to questions raised in the copious studies devoted to ionic benzene chemistry.[3]


1,5-HEXADIYNE (3600 V.)

1,5-HEXADIYNE (900 V.)

1,5-HEXADIYNE (ICR)

Figure 1. Comparison of mass spectra of 1,5-hexadiyne at various residence times; ionizing energy = 70 eV: (A) from a Hitachi RMU-6D double focusing mass spectrometer, repellers = 7 V; (B) repeller = 1 V; (C) from a Varian ICR-9 spectrometer at 1 × 10^{-7} Torr.

---

[1] H. D. Beckey, "Field Ionization Mass Spectrometry," Pergamon Press, New York, N. Y., 1971, p 143 ff.

[2] O. Osberghaus and Ch. Ottinger, *Phys. Lett.*, **16**, 121 (1965).

[3] For leading references on various aspects of this work, see H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973); T. Keough, T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, 7, 245 (1973); J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Amer. Chem. Soc.*, **94**, 6828 (1972).

Table I. Energetics for Ionization and Loss of H for 1,5-Hexadiyne[a]

Ion	Reactant	AP, eV	Method[b]	Determinations	Lit.[c]
C_6H_6	1,5-Hexadiyne[d]	9.97 ± 0.05	MS-1, -2	16	10.35
C_6H_6	1,5-Hexadiyne[d]	9.87 ± 0.03	Icr	3	
C_6H_5	1,5-Hexadiyne[d]	10.50 ± 0.04	MS-1	8	11.47
C_6H_5		10.23 ± 0.07	MS-2	8	
C_6H_5		10.24 ± 0.02	m*(1)	4	
C_6H_5		10.22 ± 0.02	m*(2)	3	
C_6H_5		10.21 ± 0.03	Icr	3	
$C_6H_4D_2$	1,5-Hexadiyne-*1,6-d_2*[e]	9.99 ± 0.04	MS-1	4	
$C_6H_4D_2$	1,5-Hexadiyne-*1,6-d_2*[e]	9.97 ± 0.06	Icr	3	
$C_6H_3D_2$	1,5-Hexadiyne-*1,6-d_2*[e]	10.53 ± 0.02	MS-1	6	
$C_6H_3D_2$	1,5-Hexadiyne-*1,6-d_2*[e]	10.18 ± 0.03	Icr	3	

[a] Semilog method used. Data acquired and reduced on line with a Varian 620/i computer; IP(furan) = 8.9 V as standard. [b] MS-1, Hitachi mass spectrometer, accelerating voltage = 3600 V, repellers = 7 V; MS-2, accelerating voltage = 1800 V, repellers = 0 V; m*(1), appearance potential of metastable ion (78 → 77) in first field-free region under MS-1 conditions; m*(2), metastable ion in first field-free region under MS-2 conditions; temperature = 65°; icr, using ion cyclotron resonance at 25°. [c] Reference 5. [d] From Chemical Samples Co.; purity = 97%. [e] Synthesized by exchanging the unlabeled compound with LiOD in D_2O; % d_2 = 98%.

Table II. Comparison of Metastable Abundances for Various Fragmentations of 1,5-Hexadiyne

	Loss of								
	CH_3[a]	CH_2D	CHD_2	C_2H_2	C_2HD	C_2D_2	C_3H_3	C_3H_2D	C_3HD_2
Obsd	1.0	3.0	1.0	6.1	7.5	1.0	1.0	3.0	1.0
Calcd[b]	1.0	3.0	1.0	6.0	8.0	1.0	1.0	3.0	1.0

[a] Methyl loss measured using normal ions at 25 eV. [b] Calculated for complete H,D scrambling.

The phenomenon is most clearly illustrated by comparing the mass spectrum A in Figure 1 (source residence time = 0.6 × 10^{-6} sec) with the low-pressure ion cyclotron resonance (icr) spectrum (cell residence time = 2 × 10^{-3} sec). At short residence time, the *m/e* 77 ion is of minor importance, and the spectrum is similar to that of benzene as has been previously pointed out.[4] At the longer times available in the icr experiment, *m/e* 77 becomes the base peak, and the molecular ion is now of minor importance. This observation, to our knowledge, is an unprecedented example of continuing ionic fragmentation.[5]

Small changes are also observed in the per cent of the total ionization for the ions in the *m/e* 52 and 39 regions which may indicate further fragmentation of these species. At 10^{-7} Torr in the icr, no detectable ion–molecule reactions are observed and the results cannot be attributed to such occurrences

To look more closely at this unusual effect, the energetics were measured under two different source conditions on our mass spectrometer as well as in the icr (Table I). First of all, we note a strikingly low activation energy for loss of H compared to the energetics for benzene. Increasing ion residence time by either using zero draw-out field or by icr shifts the appearance potential for *m/e* 77 (*m/e* 79 in the d_2 case) to lower energy by *ca.* 0.3 eV. The results suggest a slow increase in the rate constant as a function of internal excitation which gives rise to the so-called "kinetic shift."[6,7] Other fragmentations, such as the loss of H from benzene[8] and HCN from benzonitrile,[9] have been reported to give even larger "kinetic shifts" than observed here. Yet neither of these exhibit the dramatic increases in fragmentation as does 1,5-hexadiyne. In addition, two other C_6H_6 isomers were investigated (2,4-hexadiyne and 1,3-hexadien-5-yne), and the effect was absent here as well.[10]

Some comments with regard to the appearance potential measurements may be in order. Most data from conventional instruments are taken at zero draw-out to minimize stray fields in the source. We find the semilog plots at high repeller field (short residence time) shift to lower energy as would be expected. However, no significant change in curve shape can be detected. For any set of source conditions, the various curves are perfectly parallel near the threshold. In addition, the difference in the IP's of the standard and 1,5-hexadiyne is entirely independent of repeller field providing assurance that the differences in AP's are real. The curves obtained by icr are also parallel but somewhat steeper at the onset than those obtained with the mass spectrometer as has been previously noted.[7]

The extent of scrambling in the fragmentation of 1,5-hexadiyne-*1,6-d_2* was measured using defocused metastable ions. The results (Table II) show the hydrogen atoms are completely scrambled prior to losses of CH_3, C_2H_2, and C_3H_3 supporting the suggestion that substituent scrambling in benzene may occur *via* an acyclic strucuture.[11] Assuming the $C_6H_6^+$ which loses H is also scrambled, we calculate a k_H/k_D of 2.3 which is in accord with the idea that the rate curve for H loss is relatively flat in the 10^5-sec^{-1} region.[12] The excellent

---

(4) J. Momigny, L. Brakier, and L. D'Or, *Bull. Cl. Sci. Acad. Roy. Belg.*, **48**, 1002 (1962).

(5) Ionic fragmentation is known to continue at times longer than 1 μsec as evidenced by observation of metastable ions. What is unprecedented is the extent of fragmentation after 1 μsec which is observed here.

(6) W. A. Chupka and J. Berkowitz, *J. Chem. Phys.*, **32**, 1546 (1960).

(7) We have recently pointed out the advantages of icr in evaluating kinetic shift: M. L. Gross, *Org. Mass Spectrom.*, **6**, 827 (1972).

(8) M. L. Vestal, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968.

(9) I. Hertel and Ch. Ottinger, *Z. Naturforsch. A*, **22**, 40 (1967).

(10) The icr and mass spectra of the above-mentioned compounds are nearly identical. No absolute changes of greater than 10% in relative abundance are observed.

(11) M. E. Rennekamp, W. O. Perry, and R. G. Cooks, *J. Amer. Chem. Soc.*, **94**, 4985 (1972).

(12) M. Bertrand, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, **7**, 193 (1973).

agreement in appearance potentials for loss of H from C_6H_6 and $C_6H_4D_2$ (Table I) also indicates the positional integrity of various hydrogen atoms is lost in the fragmenting molecular ion.

It is difficult to understand why a simple bond cleavage reaction is subject to such dramatic fragmentation changes as are observed. One tentative explanation is that the most energetically favorable loss of H is preceded by a slow isomerization reaction, but since little change is observed for other fragmentations of 1,5-hexadiyne, isolated states would be involved. More studies are planned to clarify these points and to test related compounds for similar effects. The ion-molecule chemistry of isomeric C_6H_6 cations will be discussed in a full paper.

Acknowledgment. We thank Dr. Robert Williams and Professor C. L. Wilkins for providing the computer expertise for the energetic measurements. Helpful discussions with Dr. R. G. Cooks are appreciated.

Michael L. Gross,* Ronald J. Aerni
Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68508
Received July 30, 1973

Conformations and Energy Barriers in Medium- and Large-Ring Ketones. Evidence from ^{13}C and ^{1}H Nuclear Magnetic Resonance

Sir:

We wish to report that the ^{1}H and ^{13}C nmr spectra[1] of the C_9 to C_{16} cycloalkanones, like the spectra of the corresponding cycloalkanes,[2] are strongly temperature dependent in the range of −80 to −170°.

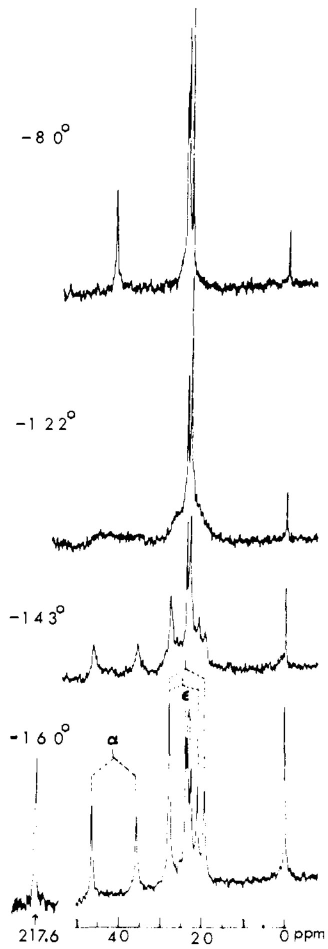
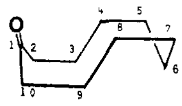
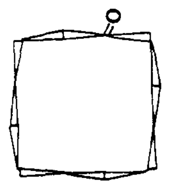


Figure 1. Carbon-13 nmr spectrum (63.1 MHz) of cyclodecanone as a 3% solution in 6:1 $CHCl_2F$–vinyl chloride at various temperatures. The carbonyl band is shown only for the spectrum at −160°. Protons are noise decoupled, and the reference is tetramethylsilane.



BCB-1

BCB-3



I

The cmr spectra of the C_9–C_{12} cycloalkanones undergo simple changes at low temperatures, as exemplified in Figure 1, which shows the cmr spectrum of cyclodecanone at various temperatures. The resonances of the carbonyl, α, and ε carbons in the room-temperature cmr spectrum of the C_{10} ketone have been assigned previously.[3] The carbonyl and ε carbon lines remain unchanged at low temperatures, in agreement with the presence of a single kind of conformation.[4] On the other hand, the α, β, and γ carbon resonances are 1:1 doublets at −160°, showing that the single conformation lacks a C_2 axis or a plane of symmetry perpendicular to the C_α—C=O plane. Thus, the BCB-1 conformation[5] (*i.e.*, boat–chair–boat[6] with the oxygen at C1) cannot be the preferred conformation of cyclodecanone. The BCB-2 and BCB-3 forms (and their mirror images) are both consistent with the nmr data, but the BCB-3 form, which has four transannular H–H repulsive interactions and has the carbonyl group at a "noncorner" position, should be highly favored over the BCB-2 form, which has six such interactions and has the carbonyl group at a "corner" position.[7] Strain energy calculations[8] indeed indicate that the BCB-3 form is of lowest energy.

The cmr spectra of the C_9, C_{11}, and C_{12} cyclic ketones show changes at low temperatures similar to those described for cyclodecanone. Thus, each of these compounds very likely exists in a single kind of conformation, having the same symmetry as mentioned above for

---

(1) The nmr spectra (63.1 MHz for ^{13}C and 251 MHz for ^{1}H) were obtained at a magnetic field of 59 kG. All cmr spectra were obtained by the Fourier-transform technique with protons noise decoupled.

(2) (a) F. A. L. Anet and J. J. Wagner, *J. Amer. Chem. Soc.*, **93**, 5266 (1971). (b) F. A. L. Anet, A. K. Cheng, and J. J. Wagner, *ibid.*, **94**, 9250 (1972); (c) F. A. L. Anet and A. K. Cheng, unpublished work.

(3) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 1347 (1970).

(4) A chiral conformation and its mirror image are taken to be of the same kind in the present discussion.

(5) The chemical shifts at room temperature in the cmr spectrum of cyclodecanone have been considered to support the BCB-1 conformation.[3]

(6) The boat-chair-boat is the preferred conformation of cyclodecane: J. D. Dunitz, *Pure Appl. Chem.*, **25**, 495 (1971).

(7) A corner position is one where the two adjacent dihedral angles have the same signs and about the same magnitudes. A methylene group at a corner position is unhindered and there is thus no relief in nonbonded interactions when that group is replaced by a carbonyl group. Furthermore, the carbonyl oxygen at a corner site is always eclipsed with two hydrogens on the α and α′ carbons; this geometry is known[8] to be higher in energy than one where the oxygen is eclipsed with a methylene group, as occurs in the BCB-3 form. In the BCB form the corner sites are 2, 5, 7, and 10.

(8) N. L. Allinger, M. T. Tribble, and M. A. Miller, *Tetrahedron*, **28**, 1173 (1972).