It is interesting to note that DMA increases the pH of the solution and shows similar spectral effects to that of increased pH. However, the time dependence is quite different in the two cases; OH^- leads to one short decay, while DMA leads to one long decay. Hence, the mechanisms of the two effects are quite different. It is intriguing to note that in the case of pyrene, the complex shows an emission which is very similar to a substituted pyrene. In other words, the single emission peak of pyrene at 3950 Å is replaced by spectrum with two peaks, one at 3900 Å and a second in the region of 3700 Å. Adsorption of dimethylaniline itself on the particle does not give rise to spectra of this type. Hence, the new emission and excitation spectra are due to the complex of DMA and pyrene on the TiO_2 surface. It is known that excitation of mixtures of DMA and pyrene leads to an exciplex formation in many solvents,[31] and that exciplex emissions are observed in hydrophobic solvents. The spectra of the exciplexes are at much longer wavelengths (λ >4600 Å) than those observed in the TiO_2 samples.

The similarity of the DMA–pyrene–TiO_2 complex emission to that of a substituted pyrene suggests that the complex alters the nature of the adsorption of pyrene on TiO_2 and the interaction of DMA with pyrene on TiO_2 is not of the exciplex type. These preliminary data indicate the unique nature of the interaction of aromatic molecules with a TiO_2 surface. Further studies are required in order to pin down specific details of the adsorption process. Studies, such as those outlined above, may be useful in probing the active sites of catalysts.

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Comprehensive Theoretical Study of Isomers and Rearrangement Barriers of Even-Electron Polyatomic Molecules H_mABH_n (A, B = C, N, O, and F)

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Abstract: Potential energy surfaces for the polyatomic neutral species H_mABH_n (A, B = C, N, O, F) are studied by ab initio molecular orbital theory. Only systems with an even number of electrons are considered. All are found to be most stable as electronic singlet states with normal structures corresponding to maximum valence. Less stable singlet isomers, with abnormal valency, are found for HNC, H_2NCH, HOCH, H_2NN, H_3NCH_2, H_3NNH, and H_3NO. Barriers for rearrangement by 1,2-hydrogen shift to the normal-valent form are estimated. Other possible 1,2-hydrogen-shifted singlet isomers, H_2CC, H_3CCH, H_3CN, H_2COH_2, H_2CFH, NOH, $HNOH_2$, HNFH, H_2OO, and HFO, either have shallow potential minima or do not correspond to minima at all. Triplet equilibrium structures, in the abnormal-valence coordination, also exist and are more stable than corresponding singlet structures for H_3CCH, H_3CN, and HON. They are separated from other triplet isomers, in the normal valence coordination, by high barriers. The theory predicts that singlet CH_2, NH, and O will insert into NH_3, OH_2, and FH without activation in all cases.

1. Introduction

The set of polyatomic compounds H_mABH_n with two nonhydrogen atoms A and B contains the parent molecules for the various kinds of AB bonds. If A and B are restricted to carbon, nitrogen, oxygen, and fluorine, the molecules are $H_3C{-}CH_3$, $H_2C{=}CH_2$, $HC{\equiv}CH$, $H_3C{-}NH_2$, $H_2C{=}NH$, $HC{\equiv}N$, $H_3C{-}OH$, $H_2C{=}O$, $H_3C{-}F$, $H_2N{-}NH_2$, $HN{=}NH$, $H_2N{-}OH$, $HN{=}O$, $H_2N{-}F$, $HO{-}OH$, and $HO{-}F$. All have been studied extensively by molecular orbital techniques and all are known experimentally. In every case, the structure consistent with the normal rules of valency is found to be the most stable.

Other structures are possible for these molecules. The unsaturated species may have triplet states corresponding to $H_2C\dot{C}{-}\dot{C}H_2$, $H\dot{C}{=}\dot{C}H$, $H_2\dot{C}{-}\dot{N}H$, $H\dot{C}{=}\dot{N}$, $H_2\dot{C}{-}\dot{O}$, $H\dot{N}{-}\dot{N}H$, and $H\dot{N}{-}\dot{O}$. Other isomers with abnormal valences can be derived, in principle, by 1,2-hydrogen shifts:

$$H_mABH_n \rightarrow H_{m-1}ABH_{n+1}$$

Some of these structures are known experimentally (e.g., HNC). Others are postulated as reactive intermediates and may also exist as singlets or triplets. Many of these isomeric forms and associated rearrangement barriers have been studied by a variety of theoretical techniques.[2]

All of the structures derived by 1,2-hydrogen shift from singly bonded normal valence forms can be represented formally as complexes of normal molecules with carbenes, nitrenes, or singlet oxygen, Scheme I. These may alternatively be represented as

Scheme I

$$H_3C{-}CH_3 \rightarrow \ddot{C}H_2{\cdots}CH_4$$

$$H_3C{-}NH_2 \rightarrow \ddot{C}H_2{\cdots}NH_3 \text{ or } \ddot{N}H{\cdots}CH_4$$

$$H_3C{-}OH \rightarrow \ddot{C}H_2{\cdots}OH_2 \text{ or } \ddot{O}{\cdots}CH_4$$

$$H_3C{-}F \rightarrow \ddot{C}H_2{\cdots}FH$$

$$H_2N{-}NH_2 \rightarrow \ddot{N}H{\cdots}NH_3$$

$$H_2N{-}OH \rightarrow \ddot{N}H{\cdots}OH_2 \text{ or } \ddot{O}{\cdots}NH_3$$

$$H_2N{-}F \rightarrow \ddot{N}H{\cdots}FH$$

$$HO{-}OH \rightarrow \ddot{O}{\cdots}OH_2$$

$$HO{-}F \rightarrow \ddot{O}{\cdots}FH$$

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(2) For a review see: Schaefer, H. F., III *Acc. Chem. Res.* 1979, *12*, 288.

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polar ylides (e.g., $H_2\bar{C}-NH_3^+$). Structures derived from multiple bonds may be written as substituted carbenes or nitrenes, Scheme II. Again polar descriptions (e.g., $\bar{C}\equiv NH^+$) may also be used.

Scheme II

$$H_2C{=}CH_2 \rightarrow H\ddot{C}{-}CH_3$$

$$HC{\equiv}CH \rightarrow :C{=}CH_2$$

$$H_2C{=}NH \rightarrow H\ddot{C}{-}NH_2 \text{ or } H_3C{-}N:$$

$$HC{\equiv}N \rightarrow :C{=}NH$$

$$HN{=}NH \rightarrow :N{-}NH_2$$

$$HN{=}O \rightarrow :N{-}OH$$

This paper presents a general theoretical survey of the structures and energies of such species. The following general questions will be addressed:

1. What are the structures of the normal valency molecules and their corresponding triplet isomers?
2. Do the isomers with abnormal valence exist as equilibrium structures, that is, as local minima on the potential surface? This question applies to both singlet and triplet forms.
3. Is the singlet or the triplet state of the abnormal valency structure lower in energy? For the unmodified CH_2, NH, and O systems, the triplet is known to be lowest but the singlet–triplet separation will clearly be changed by substitution or complexation.
4. What is the nature of the complex structures (eq 1), such as $\ddot{C}H_2\cdots OH_2$, and how strong is the binding? For example, if dissociation of $\ddot{C}H_2\cdots OH_2$ into CH_2 and OH_2 requires only a small amount of energy, the species will not have a significant lifetime.
5. If the abnormal-valent singlet structures can exist, what is the energy barrier inhibiting rearrangement to the normal-valent form?
6. Do the abnormal-valent structures which are not potential minima play a role as transition structures for degenerate 1,2-hydrogen exchange reactions?
7. How do the energies of the abnormal-valent triplets compare with the normal triplets and what is the activation barrier separating them?

Some of these topics have been discussed in previous theoretical papers, cited later in the text. The main objective of the present work is to approach the problems systematically for the whole series at a higher, uniform level of theory. All the systems mentioned above are examined, with the exception of (1) complexes involving methane and (2) some triplet structures which preliminary calculations indicate to be noncompetitive with corresponding singlets. Most of the unsaturated molecules listed above have been studied previously, an exception being the rearrangement of aminomethylene to formaldimine. Few previous studies exist of 1,2 shifts in the saturated molecules. An important general objective is to study the role of high-level correlation theory including triple substitutions on the energies of all these intramolecular rearrangements.

2. Theoretical Methods and Results

The standard theoretical procedure, applied to all compounds considered, consists of the following steps.

1. Stationary point geometries are determined at the Hartree–Fock level using the 6-31G* basis. Spin-restricted (RHF) theory is used for singlets and spin-unrestricted (UHF) for triplets. These structures and energies are denoted by HF/6-31G*.
2. A complete set of harmonic force constants is obtained for each of these stationary points.[3] These are used to test the nature of the stationary point (no negative eigenvalues for an equilibrium structure and one negative eigenvalue for a transition structure). They are also used to compute harmonic vibrational frequencies (with principal isotopes) and corresponding zero-point vibrational energies. The imaginary (reactive) frequency is omitted from the zero-point energy for transition structures.
3. Electron correlation is included in single-point calculations at the HF/6-31G* geometries. These use fourth-order Møller–Plesset theory in the space of single, double, and quadruple substitutions,[4] together with the 6-31G** basis (e.g., with polarization functions on hydrogen). This model is denoted by MP4SDQ/6-31G**//HF/6-31G*, where "//" means "at the geometry of." The inner-shell molecular orbitals are excluded from all electron correlation calculations.
4. The effect of triple substitutions on the correlation energy is also included at fourth order[5] but only with the smaller 6-31G* basis set. Preliminary studies reported elsewhere have indicated that this three-electron effect is significant.[6] This set of computations is denoted by MP4SDTQ/6-31G*.

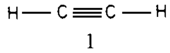
The results are summarized in Tables I and II. Table I contains the HF/6-31G* stationary-point energies, together with the bond lengths for the heavy atoms. The full structural data are presented elsewhere.[7] In Table II, the HF/6-31G** and MP4SDQ/6-31G** energies are given, together with the fourth-order triples contribution ΔE_{MP4T}. The final two columns give the zero-point energy and the energy relative to the most stable form (after zero-point correction).

One general point should be made about the interpretation of the relative energies. If two minima A and B are found on the HF/6-31G* surface together with a transition structure T, then the energy of T is necessarily higher than that of A or B. If A is the most stable form, $E(T) > E(B) > E(A)$. However, it may happen that the single-point calculation will show a different order, $E(B) > E(T) > E(A)$. Such results suggest (but do not prove) that, at higher theoretical levels, structure B is *not* a minimum and that no rearrangement transition structure exists.

3. Discussion

We discuss each system in turn, leaving general remarks to conclusions.

C_2H_2. The two isomers considered for C_2H_2 are acetylene (**1**) and vinylidene, for which a planar C_{2v} structure **2** has often been considered. In an important paper on this system,[8] Dykstra and Schaefer (DS) found separate minima for these species, separated by a planar transition structure **3**. They found a classical barrier of 8.6 kcal and an exothermicity of 40.0 kcal using configuration interaction (CISD) and a DZ+P (double-ζ + polarization) basis.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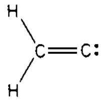
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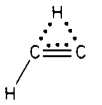
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The results of the standard procedure in this paper lead to lower barriers. At the MP4SDQ/6-31G** level, broadly comparable to the work of DS, the barrier is 6.7 kcal and the exothermicity 41.6 kcal. Triple substitutions favor acetylene and the transition structure relative to vinylidene, the corresponding barrier and exothermicity being 4.6 and 39.8 kcal. Addition of zero-point corrections reduces the barrier further to only 2.5 kcal, the exothermicity now being 41.5 kcal.

Since these standard-level studies were completed, further refinement of the C_2H_2 surface has been undertaken[9] using geometries optimized at the MP2/6-31G* level and the (triple valence

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Table I. HF/6-31G* Energies and Structural Data

stoichiometry	structure[a]	point group	AB bond length[b]	total energy[c]	Hessian index[d]
C_2H_2	$HC{=}CH$ (1)	$D_{\infty h}$	1.185	−76.817 83	0
	$H_2C{=}C{:}$ (2)	C_{2v}	1.294	−76.763 40	0
	$HC(H)C$ (3)	C_s	1.237	−76.737 17	1
C_2H_4	$H_2C{=}CH_2$	D_{2h}	1.317	−78.031 72	0
	$H_3C{-}\ddot{C}H$ (4)	C_1	1.485	−77.922 37	0
	$H_3C{-}\ddot{C}H$ (5)	C_s	1.491	−77.921 89	1
	$H_2C(H)CH$	C_1	1.378	−77.900 95	1
	$H_3C{-}\ddot{C}H$(t) (5)	C_s	1.486	−77.963 58	0
	$H_2\dot{C}{-}\dot{C}H$(t) (6)	D_{2d}		−77.964 30	0
	$H_2\dot{C}(H)\dot{C}H_2$(t)	C_1		−77.862 19	1
CHN	$HC{\equiv}N$	$C_{\infty v}$	1.133	−92.875 20	0
	$:C{=}NH$	$C_{\infty v}$	1.154	−92.855 33	0
	$C(H)N$	C_s	1.169	−92.791 95	1
	$:C{=}NH$(t)	C_s	1.271	−92.722 64	
CH_3N	$H_2C{=}NH$ (7)	C_s	1.250	−94.028 46	0
	$H_2C{=}NH$ (8)	C_{2v}	1.220	−93.976 72	1
	$H\ddot{C}{-}NH_2$ (10)	C_s	1.309	−93.974 35	0
	$H_3C{-}N{:}$	C_s	1.373	−93.906 88	0
	$H_2C(H)N$	C_s	1.288	−93.903 72	1
	$HC(H)NH$ (11)	C_1	1.321	−93.871 81	1
	$H_3C{-}N{:}$(t)	C_{3v}	1.433	−94.003 97	0
	$H_2\dot{C}{-}\dot{N}H$(t) (9)	C_s	1.402	−93.962 68	0
	$H\ddot{C}{-}NH_2$(t) (12)	C_s	1.386	−93.952 99	0
	$H_2C(H)N$(t)	C_s	1.423	−93.896 03	1
	$HC(H)NH$(t)	C_1	1.401	−93.863 62	1
CH_5N	$H_3C{-}NH_2$ (13)	C_s	1.453	−95.209 83	0
	$H_2\ddot{C}{\cdots}NH_3$ (14)	C_s	1.606	−95.092 69	0
	$H_2C(H)NH_2$ (15)	C_s	1.680	−95.049 87	1
CH_2O	$H_2C{=}O$ (16)	C_{2v}	1.184	−113.866 33	0
	$H\ddot{C}{-}OH$ (trans) (17)	C_s	1.300	−113.783 52	0
	$H\ddot{C}{-}OH$ (cis) (18)	C_3	1.298	−113.774 49	0
	$H\ddot{C}{-}OH^*$ (19)	C_1	1.347	−113.738 29	1
	$HC(H)O$ (20)	C_s	1.270	−113.699 64	1
CH_4O	$H_3C{-}OH$ (21)	C_s	1.400	−115.035 42	0
	$H_2C{\cdots}OH_2$ (22)	C_s	2.138	−114.896 62	0
	$H_2C(H)OH$	C_1	1.807	−114.872 38	1
CH_3F	$H_3C{-}F$	C_{3v}	1.365	−139.034 61	0
	$H_2C{\cdots}FH$ (23)	C_{2v}	2.898	−138.892 83	0
	$H_2C(H)F$	C_s	1.905	−138.871 91	1
H_2N_2	$HN{=}NH$ (trans) (24)	C_{2h}	1.216	−109.994 77	0
	$HN{=}NH$ (cis) (25)	C_{2v}	1.215	−109.983 50	0
	$H_2N{=}N{:}$ (26)	C_{2v}	1.215	−109.963 58	0
	$HN{=}NH$ (27)	C_s	1.207	−109.901 31	1
	$HN(H)N$ (28)	C_s	1.251	−109.846 29	1
	$H_2H{=}N{:}$(t) (29)	C_s	1.351	−109.982 83	0
	$H\dot{N}{-}\dot{N}H$(t) (30)	C_2	1.314	−109.958 60	0
H_4N_2	$H_2N{-}NH_2$ (31)	C_2	1.413	−111.169 37	0
	$H_3N{\cdots}\ddot{N}H$ (32)	C_s	1.494	−111.088 08	0
	$H_2N(H)NH$	C_1	1.638	−111.038 68	1
HNO	$HN{=}O$	C_s	1.175	−129.786 07	0
	$:N{-}OH$	C_s	1.247	−129.729 78	0
	$N(H)O$	C_s	1.273	−129.641 53	1
	$H\dot{N}{-}\dot{O}$(t)	C_s	1.231	−129.787 71	0
	$:N{-}OH$(t)	C_s	1.316	−129.797 22	0
	$N(H)O$(t)	C_s	1.299	−129.712 54	1
H_3NO	$H_2N{-}OH$ (33)	C_s	1.403	−130.978 84	0
	$H_3N{\cdots}O$	C_{3v}	1.376	−130.933 89	0
	$H\ddot{N}{\cdots}OH_2$ (35)	C_s	1.863	−130.880 97	0
	$H_2N(H)O$ (34)	C_s	1.513	−130.874 43	1
	$HN(H)OH$	C_1	1.744	−130.854 47	1
H_2NF	$H_2N{-}F$	C_s	1.386	−154.955 78	0
	$H\ddot{N}{\cdots}FH$	C_1	2.211	−154.862 43	0
	$HN(H)F$	C_1	1.789	−154.838 80	1
H_2O_2	$HO{-}OH$	C_2	1.397	−150.764 79	0
	$H_2O{\cdots}O$ (36)	C_s	1.606	−150.700 24	0
	$HO(H)O$ (37)	C_1	1.602	−150.666 41	1
HFO	$HO{-}F$	C_s	1.376	−174.729 58	0
	$O{\cdots}FH$	C_s	1.928	−174.669 99	0
	$O(H)F$	C_s	1.630	−174.637 18	1

[a] (H) denotes position intermediate between nonhydrogen atoms. (t) denotes a stationary point on the lowest triplet surface. [b] Angstroms. [c] Hartrees. [d] The number of negative eigenvalues of the matrix of energy second derivatives.

split) 6-311G** basis for the final points. The calculated activation barrier is even further reduced to only 0.9 kcal, leading to the conclusion that the vinylidene isomer will have an extremely short lifetime and may indeed itself be the transition structure for the experimentally known degenerate rearrangement in which the hydrogen nuclei of acetylene change places.[9b]

All of this is consistent with another recent study by Osamura, Schaefer, Gray, and Miller.[10] They obtain a classical barrier of

Table II. Total and Relative Energies[a]

structure	point group	E_{HF}[b]	E_{MP4SDQ}	ΔE_{MP4T}[c]	E_{vib}	E_{rel}
$HC\equiv CH$ (1)	$D_{\infty h}$	−76.821 84	−77.095 14	−0.011 10	18.5	
$H_2C=C\colon$ (2)	C_{2v}	−76.767 36	−77.028 79	−0.008 02	16.4	41.5
$HC(H)C$ (3)	C_s	−76.743 93	−77.018 04	−0.011 48	14.3	44.0
$H_2C=CH_2$	D_{2h}	−78.038 84	−78.344 14	−0.008 15	34.4	
$H_3C-\ddot{C}H$ (4)	C_1	−77.929 31	−78.219 61	−0.005 66	31.6	76.9
$H_3C-\ddot{C}H$ (5)	C_s		−78.218 86	−0.005 57	31.2	77.1
$H_2C(H)CH$	C_1	−77.910 55	−78.215 59	−0.008 61	30.9	76.9
$H_3\leftarrow\ddot{C}H$ (triplet) (5)	C_s	−77.970 42	−78.236 55	−0.004 61	31.9	67.2
$H_2\dot{C}-\dot{C}H$ (triplet) (6)	D_{2d}	−77.971 64	−78.241 21	−0.004 45	29.8	62.3
$H_2C(H)CH$ (triplet)	C_1	−77.872 17	−78.150 36		27.9	
$HC\equiv N$	$C_{\infty v}$	−92.877 14	−93.170 98	−0.012 58	11.3	
$\colon C=NH$	$C_{\infty v}$	−92.859 61	−93.145 75	−0.011 61	10.7	15.9
$C(H)N$	C_s	−92.796 66	−93.091 80	−0.013 10	7.3	45.4
$H_2C=NH$ (7)	C_s	−94.035 70	−94.360 72	−0.009 08	27.1	
$H_2C=NH$ (8)	C_{2v}	−93.985 10	−94.308 97	−0.008 88	25.0	30.5
$HC-NH_2$ (10)	C_s	−93.983 67	−94.299 58	−0.007 61	26.9	39.0
$H_3C-N\colon$	C_s	−93.912 08	−94.216 93	−0.006 59	24.4	89.1
$H_2C(H)N$	C_s	−93.912 73	−94.213 84	−0.009 24	21.9	76.2
$HC(H)NH$ (11)	C_1	−93.884 11	−94.215 48	−0.010 53	22.7	85.8
$H_3C-N\colon$ (triplet)	C_{3v}	−94.008 77	−94.287 13	−0.004 81	25.3	47.1
$H_2\dot{C}-\dot{N}H$ (triplet) (9)	C_s	−93.970 03	−94.256 07	−0.005 20	24.2	65.2
$H\dot{C}-NH_2$ (triplet) (12)	C_s	−93.962 67	−94.250 41	−0.005 24	25.3	69.8
$H_2C(H)N$ (triplet)	C_s	−93.905 27	−94.200 51	−0.006 73	21.1	96.0
$HC(H)NH$ (triplet)	C_1	−93.875 13	−94.176 87	−0.007 49	21.4	110.7
H_3C-NH_2 (13)	C_s	−95.221 85	−95.577 60	−0.006 29	43.2	
$H_2\ddot{C}\cdots NH_3$ (14)	C_s	−95.106 34	−95.461 00	−0.006 49	42.5	72.3
$H_2C(H)NH_2$ (15)	C_s	−95.068 28	−95.432 57	−0.008 32	38.3	84.8
$NH_3 + \ddot{C}H_2(^1A_1)$		−95.071 84	−95.407 82	−0.003 61	34.5	100.5
$NH_3 + \ddot{C}H_2(^3B_1)$		−95.121 02	−95.434 37	−0.003 20	34.8	83.4
$H_2C=O$ (16)	C_{2v}	−113.869 74	−114.196 30	−0.009 56	18.3	
$H\ddot{C}-OH$ (trans) (17)	C_s	−113.791 49	−114.109 58	−0.007 47	18.2	55.4
$H\ddot{C}-OH$ (cis) (18)	C_s	−113.782 74	−114.101 36	−0.007 51	17.8	60.4
$H\ddot{C}-OH$* (19)	C_1	−113.747 29	−114.060 01	−0.006 48	15.4	84.6
$HC(H)O$ (20)	C_s	−113.709 31	−114.051 24	−0.012 88	13.9	84.4
H_3C-OH (21)	C_s	−115.046 68	−115.403 77	−0.006 06	34.7	
$H_2\ddot{C}\cdots OH_2$ (22)	C_s	−114.912 89	−115.259 56	−0.004 70	30.1	86.3
$H_2C(H)OH$	C_s	−114.890 05	−115.260 39	−0.009 07	29.6	83.0
$OH_2 + \ddot{C}H_2$		−114.899 88	−115.238 14	−0.003 12	25.7	96.8
H_3C-F	C_{3v}	−139.039 73	−139.379 11	−0.006 18	26.6	
$H_2\ddot{C}\cdots FH$ (23)	C_{2v}	−138.905 00	−139.226 65	−0.003 44	20.6	91.4
$H_2C(H)F$	C_s	−138.882 49	−139.232 33	−0.008 80	20.6	84.4
$\ddot{C}H_2 + HF$		−138.887 86	−139.209 06	−0.003 18	17.5	99.5
$HN=NH$ (trans) (24)	C_{2h}	−110.001 23	−110.347 28	−0.010 09	19.7	
$HN=NH$ (cis) (25)	C_{2v}	−109.990 37	−110.338 04	−0.010 28	19.4	5.4
$H_2N-N\colon$ (26)	C_{2v}	−109.970 70	−110.306 64	−0.009 41	18.9	25.1
$HN=NH$ (27)	C_s	−109.910 26	−110.257 65	−0.012 91	16.9	51.7
$HN(H)N$ (28)	C_s	−109.859 91	−110.219 84	−0.013 92	13.8	71.6
$H_2N-N\colon$ (triplet) (29)	C_s	−109.990 36	−110.292 15	−0.005 88	18.1	35.6
$H\dot{N}-\dot{N}H$ (triplet) (30)	C_2	−109.965 96	−110.276 59	−0.007 02	17.0	43.6
H_2N-NH_2 (31)	C_2	−111.183 50	−111.558 12	−0.006 49	36.4	
$H_3N\cdots NH$ (32)	C_s	−111.101 85	−111.476 56	−0.007 24	35.5	49.8
$H_2N(H)NH$	C_1	−111.058 28	−111.444 82	−0.009 93	31.4	63.9
$NH_3 + \colon NH$		−111.049 44	−111.399 53	−0.003 36	28.4	93.4
$NH_3 + \colon NH$ (triplet)			−111.483 88			
$HN=O$	C_s	−129.789 10	−130.139 91	−0.010 90	10.1	
$\colon N-OH$	C_s	−129.735 71	−130.073 20	−0.009 65	9.9	42.5
$N(H)O$	C_s	−129.651 86	−130.019 61	−0.016 38	6.5	68.5
$H\dot{N}-\dot{O}$ (triplet)	C_s	−129.791 64	−130.111 86	−0.008 37	8.7	17.8
$\colon N-OH$ (triplet)	C_s	−129.803 80	−130.109 97	−0.006 52	9.5	20.9
$N(H)O$ (triplet)	C_s	−129.720 27	−130.046 38	−0.010 00	5.6	54.8
H_2N-OH (33)	C_s	−130.991 64	−131.370 39	−0.006 66	27.7	
$H_3N\cdots O$	C_{3v}	−130.944 04	−131.320 94	−0.007 28	28.1	31.1
$H_2N(H)O$ (34)	C_s	−130.890 61	−131.282 40	−0.010 25	23.9	49.1
$H\dot{N}\cdots OH_2$ (35)	C_s	−130.897 09	−131.263 04	−0.006 13	24.0	64.0
$HN(H)OH$	C_1	−130.873 32	−131.265 83	−0.011 12	22.4	57.5
$NH_3 + O(^1D)$		−130.852 14	−131.193 14	−0.003 26	23.2	108.9
$\ddot{N}H + OH_2$		−130.877 48	−131.226 61	−0.002 87	19.6	84.4
$NH_3 + O(^3P)$			−131.293 06			
H_2N-F	C_s	−154.962 91	−155.325 64	−0.007 10	19.1	
$H\dot{N}\cdots FH$	C_1	−154.874 98	−155.212 10	−0.003 80	13.4	67.6
$HN(H)F$	C_1	−154.850 93	−155.223 31	−0.011 06	13.2	55.9
$\ddot{N}H + FH$		−154.865 46	−155.197 51	−0.002 93	11.4	75.3
$HO-OH$	C_2	−150.776 93	−151.161 42	−0.007 17	18.4	
$H_2O\cdots\ddot{O}$ (36)	C_s	−150.712 56	−151.083 93	−0.007 54	17.5	47.5
$HO(H)O$ (37)	C_1	−150.682 58	−151.080 70	−0.012 08	14.3	43.5
$O(^1D) + OH_2$		−150.680 18	−151.020 22	−0.002 77	14.4	87.4

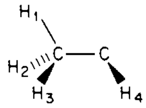
Table II (*Continued*)

structure	point group	E_{HF}[b]	E_{MP4SDQ}	ΔE_{MP4T}[c]	E_{vib}	E_{rel}
HO–F	C_s	−174.735 90	−175.106 58	−0.007 77	9.8	
HF···O	C_s	−174.678 59	−175.012 79	−0.004 64	7.2	58.3
F(H)O	C_s	−174.646 59	−175.026 76	−0.008 29	5.0	45.0
O(^{1}D) + FH		−174.668 16	−174.991 12	−0.002 83	6.2	72.0

[a] Electronic energies in hartrees; zero-point vibration energies (E_{vib}) and final relative energies (E_{rel}) in kcal/mol. [b] Using the 6-31G** basis. [c] Triples contribution. $\Delta E_{MP4T} = E_{MP4SDTQ} - E_{MP4SDQ}$ using the 6-31G* basis.

5.4 kcal, using configuration interaction and a large basis but without inclusion of triple substitutions. Including our estimate (2.1 kcal) for the lowering due to triples, the final results are in close agreement.

C_2H_4. The lowest energy isomer of C_2H_4 is ethylene, $H_2C{=}CH_2$. Shifting one hydrogen leads to ethylidene, $H_3C{-}CH$. Potential minima on the singlet HF/6-31G* surfaces are found for D_{2h} ethylene and a C_1 structure for ethylidene **4**. The dihedral angle H_1CCH_4 is 164°. If the ethylidene symmetry is constrained to the C_s staggered structure **5** (with dihedral angle H_1CCH_4 = 180°), the structure is no longer a minimum and the energy is 0.3 kcal higher (HF/6-31G*). The energy difference between singlet ethylidene and ethylene increases from 68.7 to 79.7 kcal when correlation is included at the highest level. Zero-point vibrational corrections reduce this to 77.0 kcal.



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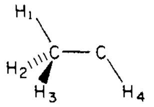

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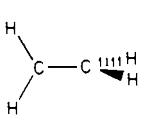
The HF/6-31G* transition structure connecting ethylene and singlet ethylidene also has C_1 symmetry. Even at this level the activation barrier for the rearrangement, ethylidene → ethylene, is found to be small (11.8 kcal). However, correlation corrections reduce the calculated activation energy to only 0.7 kcal/mol and zero-point vibrational corrections eliminate the classical barrier entirely. These results are consistent with those of a similar study. Nobes, Radom, and Rodwell[11] find a classical barrier (MP3/6-31G**//4-31G) of 2.1 kcal slightly higher than ours since triple substitutions were not included. Further work has been carried out on the ethylidene → ethylene rearrangement with the larger 6-311G** basis; this also indicates a zero barrier.[12] We conclude that singlet ethylidene is not a local minimum on the potential surface. Rather, it is likely that the C_s structure **5** is the transition structure for the degenerate rearrangement in which 1,2-hydrogens change place (Figure 1).

Two minima are found on the lowest UHF/6-31G* triplet surface. One is the D_{2d} perpendicular ethylene structure **6** and the other is triplet ethylidene which has a minimum at the C_s staggered structure **5**. After includion of electron correlation, the energy of triplet ethylene **6** lies 66.9 kcal above that of ethylene. Zero-point corrections reduce this to 62.3 kcal.



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The ethylidene triplet structure **5** is found to be less stable than **6** but to lie 9.9 kcal below the corresponding singlet **5**, using the standard methods of this paper. However, this is likely to be an overestimate, since inherent errors of ab initio theories at this level generally favor triplets. A more accurate estimate of the singlet–triplet separation in ethylidene can be obtained by evaluating the isodesmic process

$$H_3CCH\ (\text{singlet}) + CH_2\ (\text{triplet}) \rightarrow H_3CCH\ (\text{triplet}) + CH_2\ (\text{singlet})$$

At the MP4SDQ/6-31G**//6-31G* level, the reaction energy is 5.5 kcal, indicating that the singlet–triplet separation in ethylidene is less than that in methylene by this amount. Since the triplet state of CH_2 is now reasonably well established to lie below the singlet by about 9 kcal/mol,[13] we deduce that ethylidene has a triplet ground state with an energy 3–4 kcal lower than that of the singlet structure **5**. Similar results have been obtained by Harding.[10b]

The transition structure for the triplet conversion ethylidene → ethylene was sought and found (at HF/6-31G*) to be of C_1 symmetry. However, the calculated energy (MP4SDQ/6-31G**) is about 120 kcal above the singlet ethylene ground state (Figure 1). This is above the energy for the separated radicals (C_2H_3 + H), so the triplet rearrangement may well take place by dissociation/recombination.

CHN. The two closed-shell isomers, hydrogen cyanide $HC{\equiv}N$ and hydrogen isocyanide $HN{=}C{:}$, and the transition structure C(H)N connecting them have been the subject of many previous ab initio studies. All have found linear structures for both HNC and HCN and the latter to be more stable, but there has been some variation in the predicted energy differences. Pearson, Schaefer, and Wahlgren[14] determined all three geometries at the HF and CISD levels using a double-ζ + polarization basis, and found a value of 9.5 kcal for the HF isomer energy differences, but this increased to 14.6 kcal at CISD. The rearrangement potential barrier (HNC → N(H)C) fell from 40.2 kcal at HF to 34.9 kcal at CISD. Later studies were reported by Taylor, Bacskay, Hush, and Hurley[15] (HCN and HNC only) and by Redmon, Purvis and Bartlett,[16] the latter using Møller–Plesset methods.

Our MP4SDQ/6-31G*//HF/6-31G* results have also been published previously.[4] These studies all lead to the conclusion that electron correlation increases the HCN–HNC isomer energy difference from ~10 to ~15 kcal and reduces the rearrangement barrier from ~40 to ~34 kcal. The later experimental value for the isomer energy difference (14.8 ± 2 kcal[17]) agrees well with the higher theoretical results.

The studies reported in this paper are consistent with the earlier work. The 6-31G** basis is smaller than some of those used previously, but we do have estimates for contributions of triple substitutions and vibrational corrections. At HF/6-31G**, the isomer energy difference is 11.0 kcal, and this is increased to 15.8 and 16.4 kcal at MP4SDQ and MP4SDTQ, respectively. After zero-point vibrational corrections are made, the final prediction for the enthalpy difference is 15.9 kcal, in good agreement with the reported experimental value.[17]

The bridged singlet transition structure connecting HCN and HNC has a CN bond length (1.169 Å) longer than that in either

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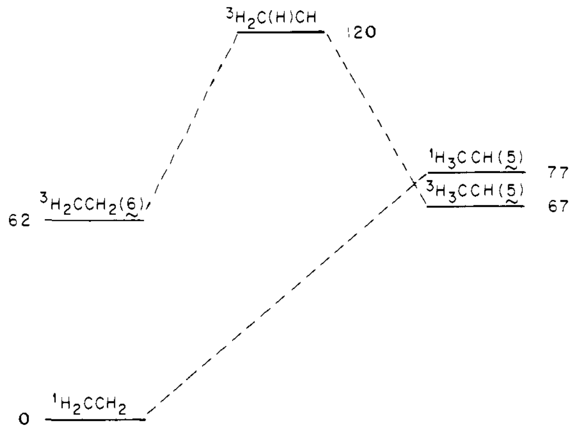


Figure 1. Energy profile for C_2H_4 (kcal/mol).

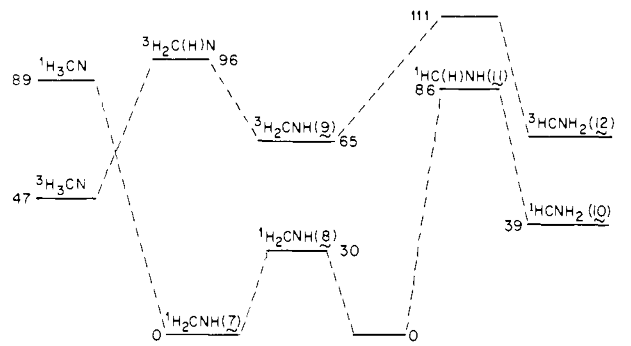
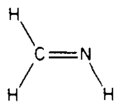


Figure 2. Energy profile for CH_3N (kcal/mol). The methylnitrene singlet structure does not correspond to a potential minimum.

isomer. Our geometries are close to those (Hartree–Fock) obtained by Pearson et al. The potential barrier for rearrangement (from HNC to HCN) is 39.5 kcal at HF/6-31G** but is lowered to 32.9 kcal when correlation is included at the highest level. Triple substitutions contribute 1.0 kcal to this lowering. Zero-point vibrational corrections lead to a final prediction of 29.5 kcal for the rearrangement activation energy. A barrier of this magnitude is consistent with the observation of both HNC and HCN in outer space.[18]

CH_3N. The maximum valence CH_3N structure is methylenimine, $H_2C{=}NH$. A single hydrogen shift could lead to two isomers, methylnitrene, $H_3C{-}N{:}$, or aminomethylene, $H_2N{-}\ddot{C}H$. Both these regions of the singlet potential surface, including the connecting transition structures, have been examined. Since the triplet surface falls below the singlet in the methylnitrene region, the corresponding triplets are included. The final results are summarized in Figure 2.

Methylenimine, $H_2C{=}NH$, is found to have a planar C_s structure **7**, consistent with previous theoretical studies.[19] The



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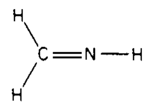

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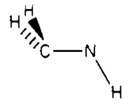
HF/6-31G* geometry compares well with experiment.[20] The transition structure for isomerization which results in exchange of the two hydrogens on carbon is found to have a planar C_{2v} geometry **8**; the predicted activation energy is 30.5 kcal. That this stereomutation takes place by planar inversion at nitrogen rather than by internal rotation around the C=N bond has been noted previously by Lehn and Munsch.[21]

Demuynck, Fox, Yamaguchi, and Schaefer (DFYS) found the ground triplet state of methylenimine to have a nonplanar transoid C_s structure **9**.[22] This $^3A''$ state has a singly occupied a″ orbital



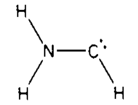
9

mainly on nitrogen and a singly occupied a′ orbital mainly on carbon. Using a configuration interaction method, these authors found the energy of triplet **9** to lie about 64 kcal above singlet **7**. Our results concur. At the MP4SDQ/6-31G** level, the energy difference is 65.7 kcal. This is increased to 68.1 kcal by triple substitutions but reduced to a final value of 65.2 kcal by vibrational corrections.

By analogy with diatomic NH, methylnitrene, $H_3C{-}N{:}$, in C_{3v} symmetry is expected to have two electrons assigned to a degenerate pair (e-type) of molecular orbitals and a triplet ($^3A_1$) ground state. This was found in our earlier paper and in the recent thorough study by DFYS. We confirm the C_{3v} triplet structure $^3A_1$ to be a local minimum in the potential surface with a relatively low energy. Our HF/6-31G* structure shows a CN bond length of 1.433 Å, somehwat shorter than the value of 1.471 Å obtained by DFYS without *d* functions. Triplet methylnitrene is found to be 18.1 kcal more stable than triplet methylenimine **4**, again in excellent agreement with DFYS (18.2 kcal). We also find (as they do) a very high activation barrier for the corresponding triplet 1,2 shift. The calculated energy of the transition structure at the MP4SDQ/6-31G**//6-31G* level is actually higher (by 6.5 kcal) than that for the separated species $H_2CN + H$ at the same level (using unrestricted UHF to the radical). The lowest energy path connecting these two triplets may thus involve dissociation.

Singlet methylnitrene in C_{3v} symmetry is expected to have ^1E symmetry and to be subject to Jahn–Teller distortion. At the HF/6-31G* level a local minimum in the potential surface (C_s symmetry) was located at a high energy. After correction for correlation and vibration, this is 89.1 kcal above the global **7**, again close to the dissociation limit. However, the transition structure connecting this minimum to methylenimine turns out to have *lower* energy after the correlation corrections are made. We therefore conclude that there is no evidence for singlet $H_3C{-}N{:}$ as a separate species. DFYS reached the same conclusion using a two-determinant wave function.

Earlier work on aminomethylene indicated a planar singlet ground state **10**, with a high degree of π delocalization from the



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nitrogen lone pair into the vacant carbene π orbital.[23] In confirmation, the π delocalization in **10** is reflected in the very short C–N bond length (1.309 Å) obtained at the HF/6-31G* level. The energy of aminomethylene is found to be 39.0 kcal above methylenimine at the highest level of theory. The transition structure (HF/6-31G*) connecting these two minima has a nonplanar geometry (**11**). The calculated energy of **11** is high

11

(85.8 kcal above methylenimine), indicating that the isomerization,

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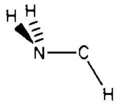
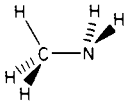
aminomethylene → methyleneimine, would require a large activation energy.

The triplet form of aminomethylene is found to have the nonplanar C_s structure **12** with a $^3A''$ electronic state. This lies


12

above the singlet state even at the Hartree–Fock level (by 13.2 kcal at 6-31G**//6-31G*). After corrections for correlation and vibrations, the singlet–triplet separation increases to 30.8 kcal. The transition structure connecting this triplet to that of methylenimine is very high in energy, again indicating that the lowest energy route for the triplet 1,2-shift may be via dissociation. Aminomethylene, or an appropriately substituted derivative, should thus have great kinetic stability as an isolated entity and should be a good candidate for experimental study. There is indeed recent experimental evidence for its existence.[24]

CH_5N. The most stable structure for CH_5N is known to be the staggered form of methylamine, $H_3C—NH_2$, **13**. The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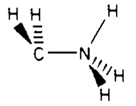
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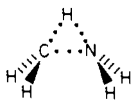
HF/6-31G* structure for **13** has already been reported and compared with experimental data.[20]

A hydrogen shift from carbon to nitrogen leads to the prototype of ylide, $H_3N^+—CH_2^-$, which may also be regarded as a complex between singlet methylene and ammonia, $H_2C\cdots NH_3$. The most stable form of this species at HF/6-31G* is the staggered structure **14**. This is a local minimum on the potential surface with a C···N bond length of 1.606 Å, somewhat longer than that found at 4-31G by Bernardi et al.[25] (1.451 Å) but comparable to that obtained in a more recent study by Eades et al.[26] (1.591 Å).

The transition structure connecting the minimum **14** with the more stable methylamine minimum **13** appears to be a C_s structure **15** with a somewhat longer bond length of 1.680 Å. The sec-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ond-derivative matrix at this geometry has one negative eigenvalue, the eigenvector corresponding to motion of the intermediate hydrogen nearly parallel to the C···N line. It may be noted that **15** is an eclipsed structure and that the C_s path **13** → **15** → **14** involves inversion at nitrogen.

The energies associated with the 1,2 shift in methylamine are shown in Figure 3, which also includes the dissociated products $CH_2(^1A_1) + NH_3$. The ylide structure **14** is predicted to be a local minimum with an energy 72.3 kcal above **13**. Eades et al.[26] obtained a comparable value of 68.7 kcal in a Hartree–Fock computation. Our results indeed show that electron correlation has little effect on the energy of this 1,2 shift.

The activation energy for the ylide rearrangement process **14** → **15** → **13** is found to be 12.5 kcal. This is large enough for the ylide to have a significant lifetime for spectroscopic observation. However, it should be noted that this barrier is lowered both by electron correlation and by vibrational corrections. The Hartree–Fock barrier (Table II) is (23.9 kcal).

15 is also the transition structure for 1,2-hydrogen exchange in methylamine, a process which might be detected experimentally by isotopic labeling. The ylide **14** would be a possible intermediate in this process. However, the calculated energy barrier (84.8 kcal) is close to the experimental C–N dissociation energy (~86 kcal).

The binding of the ylide **14** with respect to separated singlet products is 28.2 kcal. The corresponding binding energy relative to $CH_2(^3B_1) + NH_3$ is 11.1 kcal, so that **14** is bound relative to dissociation to the ground states of both separated species. The energy of the transition structure **15** is below that of the separated singlet species. Thus, the theory predicts that insertion of singlet methylene into the NH bond of ammonia (to give **13**) should proceed without activation.

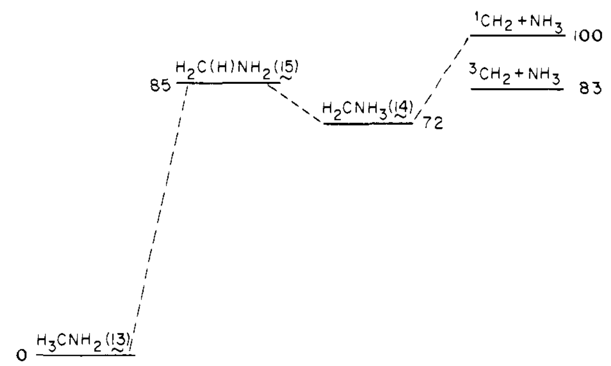


Figure 3. Energy profile for CH_5N (kcal/mol).

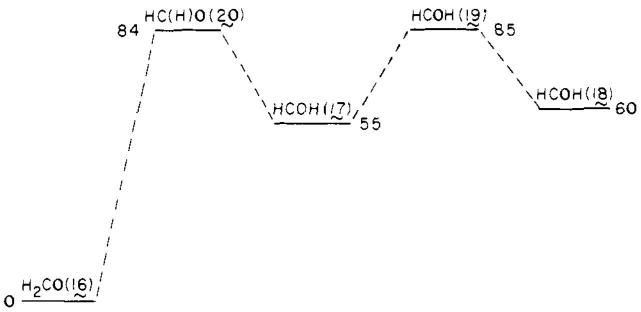
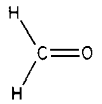


Figure 4. Energy profile for CH_2O (kcal/mol).

CH_2O. Formaldehyde, $H_2C{=}O$ (**16**) is the most stable form of CH_2O. The alternative structure is hydroxymethylene, $H\ddot{C}—OH$, which may exist in trans or cis form (**17** and **18**). Our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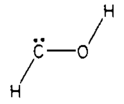
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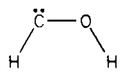
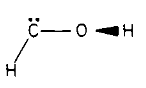

18

results on these species, excluding triple substitutions, have been reported previously[27] and are in agreement with those of comparable studies by other authors.[28] The final relative energies are illustrated in Figure 4. The trans form **17** is the second most stable isomer, 55.4 kcal above formaldehyde. The cis form **18** is 5.0 kcal higher. Some experimental evidence for the existence of an HCOH isomer has been reported.[29] Interconversion between **17** and **18** occurs by internal rotation; the transition structure **19** has C_1 symmetry and lies 29.2 kcal above the cis form. The transition structure for the 1,2 shift is the planar form **20**, 84.4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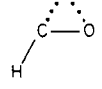
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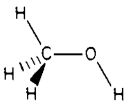
(29) Hehre, W. J., private communication.

kcal above formaldehyde. The fourth-order energy lowering from triple substitutions brings this transition structure down by 2.1 kcal relative to the formaldehyde ground state.

These MP4SDQ/6-31G** results have been extended using the 6-311G** basis and MP2/6-31G* geometries.[30] The final (zero-point corrected) energies (relative to H_2CO) are 53.1 kcal for HCOH and 81.4 kcal for the transition structure.

CH_4O. Most of the results on methanol **21** and its ylide isomer H_2C···OH_2 (**22**) have been reported previously.[27] The final relative energies listed in Table II include contributions from triple substitutions. **22** is a local minimum on the HF/6-31G* potential surface with an energy (87.1 kcal) above methanol. This is comparable with a value of 86.5 kcal found by Eades et al.[26] in a Hartree–Fock calculation. Our final number for the energy difference between **22** and **21** is 86.3 kcal, showing that electron correlation and vibrational corrections do not change the relative stability significantly.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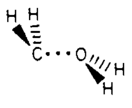
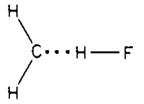

22

Although the ylide **22** is a local minimum in the Hartree–Fock potential surface, the rearrangement barrier separating **22** and **21** vanishes after corrections for electron correlation and zero-point vibrations are made. This conclusion is strengthened by the triple substitution effect, which eliminates the very small value found previously.[27] We conclude that the water–methylene complex does not exist as an equilibrium structure. It is possible that it is the transition structure for 1,2-hydrogen exchange in methanol, with an activation energy of 86.3 kcal. This is just below the experimental C–O dissociation energy in H_3COH, 91.7 kcal.[31] The energy of separated CH_2 ($^1A_1$) and H_2O lies above **22**. Consequently, insertion of singlet methylene into water to form methanol should proceed without activation.

CH_3F. The results for CH_3F differ somewhat from those for CH_4O. In addition to the methyl fluoride C_{3v} minimum, a secondary minimum **23** is found on the HF/6-31G* surface. This is planar with C_{2v} symmetry. Unlike the ylide structures for CH_5N and CH_4O, this corresponds to a complex between methylene and hydrogen fluoride in which the latter acts as a proton donor. Thus **23** is a hydrogen-bonded complex. No minimum is found for a structure with fluorine acting as an electron donor.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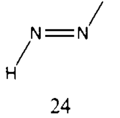
The transition structure for the rearrangement of **23** to methyl fluoride has nonplanar C_s symmetry. However, correlation corrections lower the relative energy of the transition structure substantially; the final results suggest that no barrier exists and that insertion of singlet CH_2 into HF requires no activation energy.

H_2N_2. The high-valence structure of H_2N_2 is diazene, HN=NH, which can exist in trans or cis forms (**24** and **25**). A 1,2-hydrogen shift leads to the alternative aminonitrene structure **26**. The geometries and relative energies of these species have been examined previously.[4,32] The relative energies obtained here are summarized in Figure 5. The trans form of diazene (**24**), found to be the most stable isomer, has been observed experimentally. The HF/6-31G* geometry compares well with the experimental structure.[20] The cis form (**25**) is predicted to be less stable by 5.4 kcal, in good agreement with another recent theoretical value of 4.7 kcal obtained by Casewit and Goddard.[32] These authors review the experimental literature dealing with the N_2H_2 isomers.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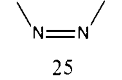
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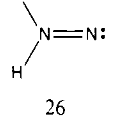
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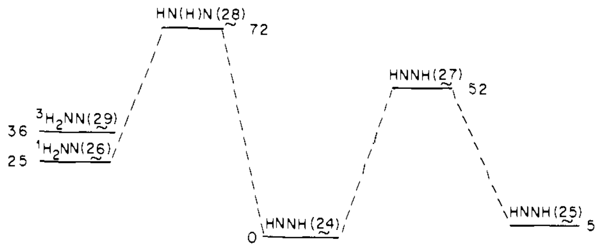
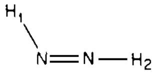


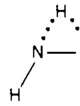
Figure 5. Energy profile for H_2N_2 (kcal/mol).

The transition structure connecting the trans and cis isomers of diazene is a planar structure **27** with valence angles H_1NN = 110.0° and H_2NN = 178.1° (the structure being slightly trans). Thus the angle H_1NN only changes slightly from its value of 107.5° in the trans form **24**. The transition structure corresponds to inversion at one nitrogen rather than internal rotation about the N=N bond. The in-plane transition structure for nitrogen inversion in methylenimine is analogous. However, the calculated NH=NH inversion barrier of 51.7 kcal is notably higher.


27

The structure of singlet aminonitrene (**26**) is found to be planar C_{2v} with two π electrons (b_1 symmetry). Note that the N–N length in this species, although formally a single bond, is as short as the double bonds in the HN=NH isomer. This bond shortening is attributed to π donation from the NH_2 group into a vacant π orbital on the nitrene nitrogen. The energy of aminonitrene is predicted to lie 25.1 kcal above *trans*-diazene, in good agreement with the value of 27.4 kcal obtained by Casewit and Goddard.[32]

A careful study was made of the singlet potential surface connecting aminonitrene and *trans*-diazene. At the HF/6-31G* level, an asymmetric transition structure of C_1 symmetry was found. If planar C_s symmetry was imposed, the resulting structure **28** was higher in energy and second-derivative studies gave two negative eigenvalues for the force-constant matrix. However, when the single-point calculations with correlation were made, the energy of the planar form **28** was lower. We conclude that the actual transition structure is planar and only this result is reported in Table II.


28

The energy of the transition structure **28** is 71.6 kcal above *trans*-diazene (**24**). This is substantially lower than the value of 83.0 kcal reported in our previous study of this system.[4] The lowering is due to (1) inclusion of hydrogen polarization functions (3.0 kcal), (2) inclusion of triple substitutions (2.4 kcal), and (3) vibrational corrections (6.0 kcal). Casewit and Goddard suggest that the isomerization **24** → **26** may occur by a dissociation–recombination pathway since they estimate the NH bond dissociation energy in **24** to be 71 kcal. The present result indicates the two processes are likely to be competitive.

We have also studied triplet states of N_2H_2 since initial Hartree–Fock studies give a triplet ground state for aminonitrene. The triplet structures examined are the 1,1 and 1,2 forms **29** and **30**.

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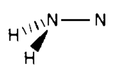

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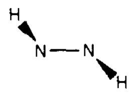
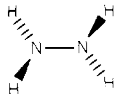


30

The 1,1 form has a nonplanar C_s structure with an angle of 129.2° between the NN bond and the HNH bisector. The 1,2 form **30** has C_2 symmetry with an HNNH dihedral angle of 96.2°.

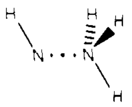
After inclusion of electron correlation, the energies of the triplet structures **29** and **30** both lie significantly above the corresponding singlets. Aminonitrene (**29**) is the more stable of the two triplets. The singlet–triplet separation for **29**, 10.5 kcal, may be compared with the value, 14.8 kcal, obtained by Davis and Goddard.[33]

H_4N_2. The most stable structure for N_2H_4 is singly bonded hydrazine (**31**) with C_2 symmetry. This symmetry also is found experimentally; the bond lengths and angles have been compared previously.[20]



31

A 1,2-hydrogen shift in **31** leads to the ammonia–nitrene complex $H_3N\cdots NH$. Exploration of this region of the potential surface leads to a C_s staggered structure **32** which lies 49.8 kcal above the global minimum **31**. The quite short NN bond length in **32** indicates a relatively strong donor–acceptor interaction. According to the energies listed in Table II, the binding relative to the separated species, singlet nitrene + ammonia, is 43.6 kcal. However, the true value is probably somewhat smaller, since our treatment uses real wave functions for the $^1\Delta$ state of NH. Thus the highest occupied orbital used is π_x (z axis along the internuclear line), rather than $\pi_x + i\pi_y$ which is appropriate to $^1\Delta$ symmetry. Actually, the singlet complex is indicated to be slightly unstable relative to dissociation into triplet nitrene + ammonia (Table II).



32

Rearrangement from the singlet $H_3N\cdots NH$ complex to H_2N-NH_2 is hindered by a significant calculated barrier of 14.1 kcal, the transition structure being of C_1 symmetry.

HNO. The HNO and NOH isomers have been studied previously in some detail by Bruna and others.[34] Our results, at somewhat lower calculated total energies, parallel theirs. The most stable structure is the singlet form HN=O with two π electrons. However, this conclusion is not reached unless electron correlation is included; triplets are favored otherwise.

A 1,2-hydrogen shift on the singlet surface leads to the hydroxynitrene structure HO–N:, again with two π electrons. This is predicted to lie 42.5 kcal above HN=O. However, this is quite close to the energy of dissociation to NO($^2\Pi$) + H(^2S), which is known to be 50 kcal.[31]

Triplet structures ($^3A''$ with three π electrons) have been located for both HNO and HON. They are close in energy, the HNO isomer being slightly more stable. Triplet HNO lies 17.8 kcal above the corresponding singlet. The HON triplet lies at 20.9 kcal, considerably below the HON singlet. Thus hydroxynitrene has a triplet ground state, significantly bound relative to NO + H.

Transition structures were determined for both singlet and triplet surfaces. The calculated energies, however, both lie above that of the separated species NO + H. We deduce that the triplet isomerization occurs by dissociation–recombination.

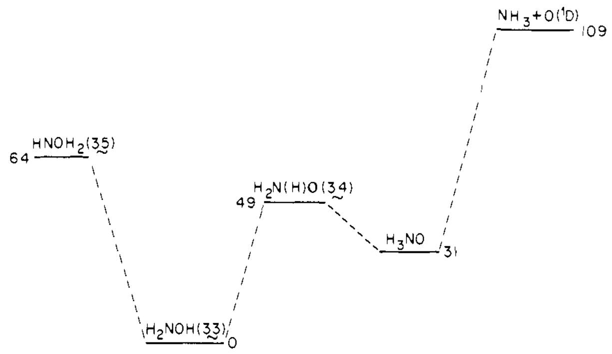
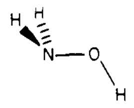


Figure 6. Energy profile for NH_3O (kcal/mol).

H_3NO. H_3NO is found to be most stable as singlet hydroxylamine, H_2NOH, in a trans form **33**. The HF/6-31G* equilibrium geometry has been compared with experiment previously, the principal deviation being in the NO bond length which is found to be 0.054 Å too short at this level.[20]



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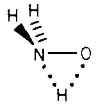

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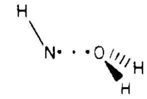
Formal 1,2 hydrogen shifts give two alternative isomers, ammonia oxide, $H_3N\cdots O$, and a nitrene–water complex. Our results are summarized in Figure 6. Ammonia oxide has the expected C_{3v} structure. It has been noted previously that the N···O bond length is sensitive to the presence of d functions in the basis set.[35] The energy of ammonia oxide, at the highest level, is predicted to be 31.1 kcal above hydroxylamine. Rearrangement to NH_2OH proceeds via a C_s transition structure **34** and requires a significant activation energy of 18.0 kcal. $H_3N\cdots O$ is also predicted to be stable relative to dissociation into ammonia and a singlet oxygen atom (D). The dissociation energy of 77.8 kcal, given from the final column of Table II, is undoubtedly too large, since real wave functions are used for the ^1D atom. However, the theory also predicts stability of $H_3N\cdots O$ relative to ammonia + oxygen (^3P). We conclude that this species, as an isolated entity, should have a significant lifetime once formed.

The other 1,2-hydrogen shifted isomer, $HN\cdots OH_2$, is predicted (HF/6-31G*) to have a trans structure **35**. The corresponding transition structure for rearrangement has C_1 symmetry. However, after correlation corrections are included, the energy of the transition structure becomes less than that of $HN\cdots OH_2$. Hence, **35** should rearrange to **33** without activation.



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Since **35** lies above **34**, 1,2-hydrogen exchange in hydroxylamine should have **34** as a transition structure, the activation barrier being 49.1 kcal, well below the N–O dissociation limit (experimental value 64.4 kcal[31]).

H_2NF. The ground state of H_2NF has a nonplanar minimum with C_s symmetry in agreement with previous studies at a lower theoretical level.[23] An alternative ylide-type structure $HN\cdots HF$ with a twisted geometry (C_1 symmetry) is found at HF/6-31G*. The transition structure for rearrangement also has C_1 symmetry. However, as addition of electron correlation eliminates the barrier for this process, we conclude that there is no second isomer on the H_2NF singlet surface.

H_2O_2. The HF/6-31G* geometry for hydrogen peroxide is twisted (C_2 symmetry) in agreement with experiment, although

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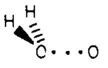
[33] Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 7111.

[34] (a) Bruna, P. J.; Marian, C. M. *Chem. Phys. Lett.* **1979**, *67*, 109. (b) Adams, G. F.; Bent, G. D.; Bartlett, R. J.; Purvis, G. D. In "Potential Surfaces and Dynamic Calculations"; Fruhlar D. G., Ed.; Plenum: New York, 1981.

[35] Radom, L.; Binkley, J. S.; Pople, J. A. *Aust. J. Chem.* **1977**, *30*, 699.

the predicted O–O length is far too short (1.393 vs. 1.475 Å) at this level. The alterantive structure obtained by 1,2-hydrogen shift is water oxide, $H_2O\cdots O$. At HF/6-31G*, this has a nonplanar (C_s symmetry) structure **36** with a long $O\cdots O$ length of 1.606 Å. The transition structure for rearrangement to HOOH has C_1 symmetry, **37**. On the HF/6-31G* surface, the rearrangement barrier is quite large (21.2 kcal). However, addition of correlation corrections at the MP4SDQ/6-31G** level reduces this to 2.0 kcal; subsequent addition of the triple substitution correction eliminates the barrier entirely. We conclude that water oxide cannot exist. It may represent the transition structure for 1,2-hydrogen exchange in hydrogen peroxide. However, this would be difficult to detect experimentally since the predicted energy of **36**, 47.5 kcal, is close to the energy of dissociation to 2(OH), known to be about 51 kcal.[31]



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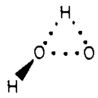

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HOF. This species has similar properties to hydrogen peroxide. HF/6-31G* theory finds HOF to be a minimum but errs in the OF bond length (1.375 vs. 1.442 Å experimentally). A second singlet isomer $HF\cdots O$ can be located at the HF/6-31G* level, but additionof correlation corrections eliminates the barrier to rearrangement.

4. Conclusions

The following conclusions may be drawn.

1. Consistent with experimental observation, theory confirms that the H_mABH_n singlet structure with normal valency corresponds to the lowest potential minimum for all the species considered.

2. For the unsaturated systems, additional singlet equilibrium structures with abnormal valency are found for HNC, H_2NCH, HOCH, and H_2NN. The corresponding rearrangement barriers are fairly high (30, 47, 29, and 47 kcal, respectively). Among the remaining systems, singlet H_2CC and H_3CCH may be very shallow potential minima, but they are effectively transition structures for degenerate hydrogen rearrangement reactions and are unlikely to be observed experimentally.

3. For the saturated systems, significant secondary singlet equilibrium structures are found for H_3NCH_2, H_3NNH, and H_3NO. Corresponding rearrangement barriers are moderate in energy (13, 14, and 18 kcal respectively). These species are all complexes of ammonia. Similar complexes involving water and hydrogen fluoride are not found to correspond to potential minima.

4. Triplet equilibrium structures, in the abnormal valence coordination, exist and lie below the corresponding singlet surfaces for H_3CCH, H_3CN, and HON. The structures of H_3CN and HON are global minima for their lowest triplet potential surfaces. Other triplet equilibrium structures are found in the normal valence coordination, H_2CCH_2, H_2CNH, and HNO. The barriers separating the different triplet isomers are high and comparable with the hydrogen dissociation energies.

5. For the saturated systems, the bound ylide-type complexes (H_3NCH_2, H_3NNH, and H_3NO) are stable with respect to separation of CH_2, NH, or O, even in the triplet forms. The rearrangement transition structures all have energies below those of separated singlet species. For the other systems (H_2OCH_2, H_2ONH, H_2OO, $HFCH_2$, HFNH, and HFO), no equilibrium structures are found. It follows that the theory predicts that singlet CH_2, NH, and O will insert into NH_3, OH_2, and FH without activation in all cases. The symmetry-constrained optimized structures H_2OCH_2 and H_2OO are probably transition structures for 1,2-hydrogen exchange, but the activation barriers are close to the dissociation limits.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 81-01061-01). It was also aided by an award from the Alexander von Humboldt Foundation.

Registry No. **1**, 74-86-2; **2**, 2143-69-3; **4**, 4218-50-2; **7**, 2053-29-4; **10**, 35430-17-2; **13**, 74-89-5; **16**, 50-00-0; **21**, 67-56-1; **24**, 15626-43-4; **25**, 15626-42-3; **26**, 35337-54-3; **27**, 3618-05-1; **31**, 302-01-2; **33**, 7803-49-8; $H_2C{=}CH_2$, 74-85-1; $HC{\equiv}N$, 74-90-8; $:C{=}NH$, 85613-19-0; $H_3C{-}N:$, 27770-42-9; $H_2C:$, 2465-56-7; $H\ddot{C}{-}OH$, 19710-56-6; OH_2, 7732-18-5; $H_3C{-}F$, 593-53-3; FH, 7664-39-3; :NH, 13774-92-0; $HN{=}O$, 14332-28-6; $:N{-}OH$, 35337-59-8; $H_3N{=}O$, 38544-48-0; $H_2N{-}F$, 15861-05-9; $HO{-}OH$, 7722-84-1; O_2^-, 16833-27-5; $HO{-}F$, 14034-79-8; H_3N, 7664-41-7.

J. Am. Chem. Soc. **1983**, *105*, 6399-6405 6399

Dioxygen Activation by Photoexcited Copper Atoms

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Received January 19, 1983

Abstract: $^2P \leftarrow {}^2S$ photoexcited Cu atoms react with O_2 in mixed rare gas/O_2 matrices to form CuO_2, which is found from UV-visible absorption/fluorescence, infrared, and electron spin resonance to be spectroscopically and chemically distinct from mono(dioxygen)copper, $Cu(O_2)$, the latter being the product of the reaction of ground-state ^2S Cu atoms with dilute rare gas/O_2 matrices. CuO_2 reacts with excess oxygen under cryogenic conditions to form copper ozonide, $Cu(O_3)$, and ozone, O_3, whereas $Cu(O_2)$ yields bis(dioxygen)copper, $Cu(O_2)_2$. The bonding between the copper and oxygen atoms in CuO_2 can be described as the interaction between a Cu^{2+} and two equivalent O^- ions, having covalent contributions to the Cu–O bonding, in contrast to $Cu(O_2)$, which is formulated as an interaction between Cu^+ and O_2^- ions, a tight-ion pair, having nonequivalent oxygen atoms with the odd electron residing mainly on the dioxygen moiety, that is, mono-η^1-superoxocuprous(I). Attention is focused on mechanistic aspects of the copper atom–dioxygen photochemical reaction, especially the differences in the reactivity of the Cu atom in its ground ^2S and excited ^2P and ^2D electronic states. It is proposed that the generation of CuO_2 following the $^2P \leftarrow {}^2S$ photoexcitation of Cu atoms in the presence of nonnearest neighbor O_2 molecules involves $^2P \rightarrow {}^2D$ relaxation, diffusion of a long-lived Cu ^2D atom to an O_2 molecule, and insertion of a Cu ^2D atom into O_2 to yield CuO_2. This should be contrasted with ^2S Cu atoms reacting spontaneously with a neighboring O_2 molecule via electron transfer to form $Cu(O_2)$.

Introduction

The known chemical reactions of group 1B metal atoms in their *ground electronic states* with dioxygen under matrix isolation conditions are summarized in Scheme I, where stoichiometric and structural assignments and bonding conclusions have been generally drawn from a combination of metal and oxygen concentration experiments, $^{16}O/^{18}O$ isotopic labeling studies with UV-visible absorption, infrared, and ESR spectroscopic detection.[1-6]

In earlier studies from this laboratory the photoprocesses of copper and silver atoms in rare gas,[7,8] methane,[9] and mixed rare gas/hydrogen[10] matrices have been discussed. A common feature of these systems is that whereas optical and ESR studies indicate that the entrapped metal atom in its ground electronic state (ns^1, $^2S_{1/2}$) is relatively unperturbed, optical excitation to the first resonance excited state (np^1, $^2P_{3/2,1/2}$) results in strong guest–host interactions, which are manifested in perturbed fluorescence spectra, photoinduced diffusion and aggregation processes, or chemical reactivity.[7-10]

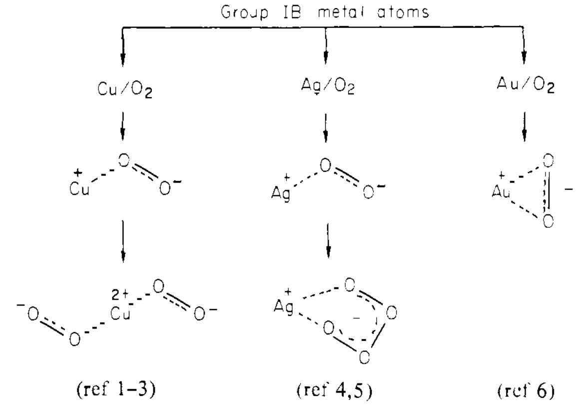
In this paper, the results of an investigation of the photochemistry of copper atoms in mixed rare gas/O_2 matrices are described. This system differs from those considered previously[9,10] in that, for the Cu/O_2 system, chemical reactivity is important for both the ground and excited electronic states of the metal atom, but of a quite different type.

Experimental Section

The experimental arrangement for matrix preparation and UV-visible absorption/fluorescence, infrared, and ESR studies have been described previously.[8,11] Copper wire (99.99%, 0.010-in. diameter) was supplied by A.D. McKay, New York, and research-grade Ar, Kr, Xe, and $^{16}O_2$ gases were supplied by Matheson of Canada. Stohler Isotopes of Montreal supplied the $^{18}O_2$ (95% enriched). Absorption spectra were recorded on a Unicam SP 8000 spectrometer, fluorescence spectra (230-900nm) on a Perkin-Elmer MPF 44B fluorescence spectrometer (both the excitation and emission wavelengths being selected with scanning monochromators), infrared spectra (4000–250 cm^{-1}) on a Perkin-Elmer 180, and X-band ESR spectra (0-6000G) on a Varian E4. The photolysis source was a 1000 W Xe arc lamp and Shoeffel Model GM 100 monochromator.

UV-Visible Absorption, Fluorescence, and Infrared Studies

Scheme I



Copper atom matrix cocondensation reactions with molecular dioxygen have been studied by UV-visible absorption,[1] infrared,[1,2] and ESR[3] spectroscopy. The occurrence of a bis(dioxygen)copper complex, $Cu(O_2)_2$, is well established and forms most readily in oxygen-rich matrices (e.g., $O_2/Ar \simeq 1{:}1 - 1{:}10$) and is characterized by an intense LMCT optical absorption around 295 nm, as illustrated in Figure 1A,B, and a ν_{OO} stretching mode around 1100 cm^{-1}. There is also evidence to indicate that in higher dispersion oxygen/rare gas matrices (e.g., $O_2/Ar \simeq 1{:}10{-}1{:}50$) the mono(dioxygen)copper complex, $Cu(O_2)$, also forms and is characterized by an optical absorption around 224 nm, Figure 1B,D, and a ν_{OO} stretching mode around 1000 cm^{-1}. A dioxygen complex, in the context of the present study, is defined as one in which molecular dioxygen is bound as a unit, with a strong bond persisting between the oxygen atoms. Both nonlinear, end-on and symmetric, side-on structures have been suggested for metal atom–O_2 complexes.[1-6,38]

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