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A Theoretical Study of Propadienone and Its Isomers Propynal and Cyclopropenone

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Abstract: Ab initio molecular orbital calculations with 4-31G and 6-31G** basis sets have been used to obtain optimized geometries for the H_2C_3O isomers, propadienone, propynal, and cyclopropenone, and a number of smaller related systems. Calculated vibrational frequencies of the H_2C_3O isomers are reported. The equilibrium structure of propadienone is found to be planar with C_{2v} symmetry, but the presence of several low-frequency vibrations allows easy distortion from such a structure. The dissociation of propadienone into vinylidene and carbon monoxide has also been examined and the transition structure for this dissociation found to resemble a weak complex of vinylidene and CO. Improved energy comparisons have been obtained by using a triple-ζ plus polarization basis set and by incorporation of electron correlation by means of the SCEP procedure. The three H_2C_3O isomers have similar energies in the order propynal < propadienone < cyclopropenone. The dissociation of propadienone is predicted to require activation energy of about 32 kcal mol^{-1}. Propadienone is predicted to be more stable than vinylidene and CO but less stable than acetylene and CO.

Introduction

During the last few years, Brown and co-workers have generated pyrolytically a series of methyleneketenes including the parent system propadienone.[2] Detailed experimental characterization of propadienone has, however, proven difficult. Its microwave spectrum has been recorded,[2f] but the interpretation in terms of structure has not been straightforward. No thermochemical data have yet been obtained for propadienone.

Under such circumstances, theoretical calculations, which can be expected to handle evanescent species such as propadienone equally as well as normal stable molecules, should be able to play a useful role. In a previous paper,[3] fairly modest levels of ab initio molecular orbital theory were used to predict a structure for propadienone and to examine its dissociation into acetylene and carbon monoxide. In this paper, we attack these problems by using much larger basis sets and with the inclusion of electron correlation in the treatment. In addition, a prediction is made of the vibrational frequencies of propadienone. Finally, we have examined in somewhat less detail other isomers on the H_2C_3O surface, namely, propynal and cyclopropenone.

Method and Results

Standard ab initio molecular orbital calculations were carried out by using the GRADSCF program.[4] Calculations were performed for a range of basis sets, namely, the split-valence 4-31G basis,[5] the split-valence plus polarization 6-31G** basis[6] and a Dunning-contracted triple-ζ plus polarization (TZdp) basis set.[7,8]

Optimized geometries were obtained by using an analytical gradient procedure.[9] The methods used for locating equilibrium geometries and predicting vibrational frequencies have been described previously.[9,10] The geometry optimization utilized the rapidly convergent method of Murtaugh and Sargent.[11] The matrix of second derivatives required for the calculation of the force constants and the vibrational frequencies was obtained by the numerical differentiation of the gradient vector. The vibrational frequencies and normal modes were determined by diagonalization of the mass-weighted force constant matrix.[10,12] Ab initio calculations at the Hartree–Fock level have been previously shown to be quite reliable for predicting molecular geometries[13] and vibrational frequencies.[14]

Electron correlation was treated by using the method of self-consistent electron pairs (SCEP).[15,16] The basic SCEP method yields a variational wave function which includes singly and doubly substituted configurations relative to a closed-shell reference configuration. Closed-shell quadruply substituted configurations constructed from approximate natural orbitals were also included in the wave function.[17] Large-scale treatments of electron correlation are possible with SCEP and in this work, SCEP wave functions spanned configuration spaces as large as 178 558 symmetry-adapted configurations.[18] The carbon and oxygen 1s atomic orbitals were frozen to substitution in the SCEP calculations and a Dunning-contracted double-ζ plus d-polarization (DZd) basis set[19,20] was used.

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[1] (a) Polyatomics Research Inc. (b) University of Illinois; (c) Australian National University.

[2] (a) Brown, R. F. C.: Eastwood, F. W.; Harrington, K. J. *Aust. J. Chem.* **1974**, *27*, 2373. (b) Brown, R. F. C.; McMullen, G. L. *Ibid.* **1974**, *27*, 2385. (c) Baxter, G. J.; Brown, R. F. C.; McMullen, G. L. *Ibid.* **1974**, *27*, 2605. (d) Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 7421. (e) Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *Aust. J. Chem.* **1977**, *30*, 179. (f) Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L. *J. Mol. Spectrosc.* **1977**, *68*, 488. (g) Blackman, G. L.; Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; McMullen, G. L.; Robertson, M. L. *Aust. J. Chem.* **1978**, *31*, 209. (h) Baxter, G. J.; Brown, R. F. C.; Eastwood, F. W.; Gatehouse, B. M.; Nesbit, M. C. *Ibid.* **1978**, *31*, 1757. (i) Brown, R. D.; Brown, R. F. C.; Eastwood, F. W.; Godfrey, P. D.; McNaughton, D. *J. Am. Chem. Soc.* **1979**, *101*, 4705. (j) Godfrey, P. D.; McNaughton, D. Paper MA7, Proceedings of the Seventh Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, 1978. (k) Brown, R. D. personal communication. We thank Professor Brown for passing on this formation.

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[8] (10s 6p 1d/5s 1p) contracted to [5s 3p 1d/3s 1p] with polarization function exponents $\alpha_d(C) = 0.8$, $\alpha_d(O) = 0.9$, and $\alpha_p(H) = 1.1$.

[9] (a) Komornicki, A.; Ishida, K.; Morokuma, K.; Ditchfield, R.; Conrad, M. *Chem. Phys. Lett.* **1977**, *45*, 595; (b) McIver, J. W.; Komornicki, A. *Ibid.* **1971**, *10*, 303.

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[12] Wilson, E. B.; Decius, J. C.; Cross, R. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955.

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[14] Pulay, P. "Methods of Electronic Structure Theory"; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Volume 4, Chapter 4.

[15] Dykstra, C. E.; Schaefer, H. F.; Meyer, W. *J. Chem. Phys.* **1976**, *65*, 2740.

[16] Dykstra, C. E. *QCPE* **1978**, *11*, 346.

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[18] For propynal with C_s symmetry, there were 114 162 A′ singly and doubly substituted configurations and 64 395 A′ quadruply substituted configurations.

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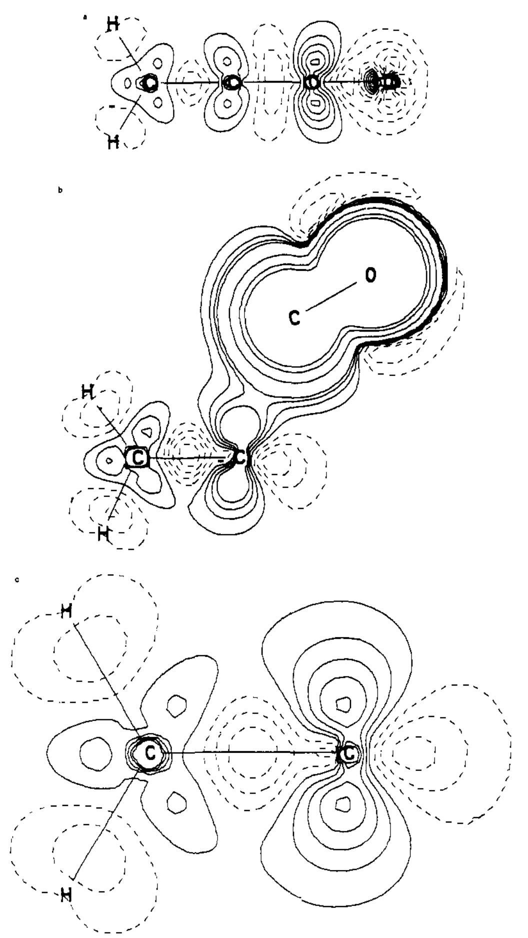
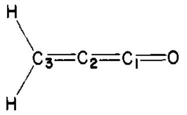


Figure 1. Electron density difference (SCEP less SCF) plots for (a) propadienone, (b) the transition structure **4**, and (c) vinylidene. Solid lines represent contours in regions where correlation increases electron density while broken lines represent contours in regions where correlation reduces the electron density. Contour spacings are 0.0025 (for a and c) and 0.0015 (for b) electrons/bohr^3.

Calculations were carried out for the H_2C_3O isomers propadienone (**1**), propynal (**2**), and cyclopropenone (**3**), the transition structure (**4**) for the dissociation of propadienone and the related



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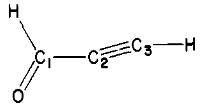

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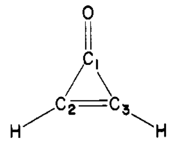
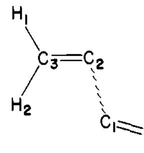


3



4

smaller systems vinylidene, acetylene, carbon monoxide, ethylene, allene, carbon dioxide, formaldehyde, and ketene. Optimized geometries are displayed in Table I, vibrational frequencies in Table II, total energies in Table III, relative energies in Table IV, and dipole moments in Table V. Density difference (SCEP less SCF) plots, designed to examine the effects of electron correlation, were prepared with the Jorgensen plotting program[21] and are shown in Figure 1 for propadienone (**1**), the transition state (**4**), and vinylidene.

Table I. Theoretical and Experimental Structural Parameters (Angles in Deg; Distances in Å)

molecule	parameter	4-31G	6-31G**	exptl[a]
propadienone (1)	C_3-C_2	1.301	1.304	
	C_2-C_1	1.260	1.269	
	C_1-O	1.177	1.154	
	C_3-H	1.075	1.079	
	$\angle HCH$	115.9	116.2	
propynal (**2**)	C_3-C_2	1.190	1.188	1.209[b]
	C_2-C_1	1.437	1.460	1.445
	C_1-O	1.210	1.184	1.215
	C_1-H	1.080	1.090	1.106
	C_3-H	1.052	1.058	1.055
	$\angle OC_1H$	120.4	121.8	122.4
	$\angle OC_1C_2$	124.1	123.5	123.7
	$\angle C_1C_2C_3$	179.6	178.4	178.4
	$\angle C_2C_3H$	179.9	179.5	180.0
	$\angle C_1C_2C_3H$	180.0	180.0	
	$\angle HC_1C_2C_3$	0.0	0.0	0.0
cyclopropenone (**3**)	C_1-C_2	1.420	1.412	1.412[c]
	C_2-C_3	1.334	1.328	1.302
	C_1-O	1.209	1.188	1.212
	C_2-H	1.062	1.071	1.097
	$\angle HC_2C_3$	152.3	152.8	152.5
transition structure (4)	C_3-C_2	1.313	1.312	
	C_2-C_1	1.922	1.937	
	C_1-O	1.129	1.112	
	C_3-H_1	1.074	1.079	
	C_3-H_2	1.067	1.071	
	$\angle H_1CC$	115.1	113.7	
	$\angle H_2CC$	127.7	128.7	
	$\angle C_3C_2C_1$	111.6	110.3	
	$\angle C_2C_1O$	140.7	142.3	
	$\angle C_3C_2C_1O$	180.0	180.0	
vinylidene	$C-C$	1.295	1.293	
	$C-H$	1.074	1.078	
	$\angle HCH$	118.4	119.8	
acetylene	$C-C$	1.189	1.186	1.203[d]
	$C-H$	1.050	1.056	1.061
carbon monoxide	$C-O$	1.128	1.114	1.128[e]
ethylene	$C-C$	1.317	1.316	1.339
	$C-H$	1.074	1.076	1.085
	$\angle HCH$	116.0	116.2	117.8
allene	$C-C$	1.294	1.296	1.308
	$C-H$	1.073	1.076	1.087
	$\angle HCH$	117.0	118.0	118.2
carbon dioxide	$C-O$	1.158	1.143	1.162
formaldehyde	$C-O$	1.206	1.184	1.205
	$C-H$	1.081	1.093	1.111
	$\angle HCH$	116.3	115.6	116.1
ketene	$C-C$	1.298	1.305	1.314
	$C-O$	1.164	1.145	1.161
	$C-H$	1.068	1.071	1.079
	$\angle HCH$	119.8	121.6	122.3

[a] Unless otherwise noted, from ref 3. [b] Reference 24. [c] Reference 25. [d] Lafferty, W. J.; Thibault, R. J. *J. Mol. Spectrosc.* 1964, *14*, 79. [e] Gilliam, O. R.; Johnson, C. M.; Gordy, W. *Phys. Rev.* 1950, *78*, 140.

Discussion

Structural Considerations. In a previous paper,[3] advantage was taken of the systematic nature of the errors in STO-3G and 4-31G structures to obtain a predicted r_0 structure for propadienone. This structure (C_3-C_2 = 1.316 Å, C_2-C_1 = 1.280 Å, C_1-O = 1.174 Å, C_3-H = 1.092 Å, <HCH = 117.1°) yielded rotational constants (A = 288.9, B = 4.17, C = 4.11 GHz) which differ significantly from subsequently reported[2f] experimental values (B = 4.38, C = 4.26 GHz). Examination of the data presented in Table I for molecules whose structures are experimentally known shows that 6-31G** geometries also have systematic errors. For example, C=C and C—H lengths are consistently underestimated.

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(19) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(20) (9s 5p 1d/4s) contracted to [4s 2p 1d/2s] with polarization function exponents as in ref 8.

(21) Jorgensen, W. L. *QCPE* **1977**, *10*, 340.

Table II. Calculated Vibrational Frequencies (4-31G, cm^{-1}) for H_2C_3O Isomers and Transition State 4

			frequency		
molecule, symmetry	vibration		theor[a]	theor[b]	exptl
propadieneone (**1**),[c] C_{2v}	a_1	ν_1	3279	2951	
		ν_2	2480	2232	
		ν_3	1908	1717	
		ν_4	1628	1465	
		ν_5	994	895	
	b_1	ν_6	1192	1073	
		ν_7	707	636	
		ν_8	246	221	
	b_2	ν_9	3356	3020	
		ν_{10}	1196	1076	
		ν_{11}	472	425	
		ν_{12}	145	131	
propynal (**2**), C_s	a′	ν_1	3662	3296	3326[d]
		ν_2	3255	2930	2858
		ν_3	2404	2164	2106
		ν_4	1893	1704	1697
		ν_5	1559	1403	1389
		ν_6	1053	948	944
		ν_7	911	820	650
		ν_8	718	646	614
		ν_9	274	247	205
	a″	ν_{10}	1146	1031	981
		ν_{11}	964	868	693
		ν_{12}	387	348	261
cyclopropenone (**3**), C_{2v}	a_1	ν_1	3506	3155	
		ν_2	2000	1800	
		ν_3	1674	1507	
		ν_4	1152	1037	
		ν_5	923	831	
	a_2	ν_6	1109	998	
	b_1	ν_7	876	788	
		ν_8	553	498	
	b_2	ν_9	3467	3120	
		ν_{10}	1295	1166	
		ν_{11}	996	896	
		ν_{12}	563	507	
transition structure (4),[e,f] C_s	a′	ν_1	3450	3105	
		ν_2	3332	2999	
		ν_3	2270	2043	
		ν_4	1789	1610	
		ν_5	1489	1340	
		ν_6	986	887	
		ν_7	456	410	
		ν_8	219	197	
	a″	ν_9	1078	970	
		ν_{10}	701	631	
		ν_{11}	170	153	

[a] Directly calculated frequencies. [b] Values scaled by 0.9 as an empirical correction to the harmonic approximation, see text. [c] Calculated zero-point vibrational energy = 8802 cm^{-1} = 25.2 kcal mol^{-1}. [d] From Brand, J. C. D.; Callomon, J. H.; Watson, J. K. G. *Discuss. Faraday Soc.* 1963, *35*, 175. [e] Calculated zero-point vibrational energy = 7970 cm^{-1} = 22.8 kcal mol^{-1}. [f] Frequency in negative curvature direction = 375i cm^{-1}.

The 6-31G** structure for propadienone may be corrected for such deficiencies, and this procedure leads to a structure which is not significantly different from the previous predicted structure.[3] The discrepancy between the experimental rotational constants and those derived from the empirically estimated r_0 structures is sufficiently large that the changes that would need to be made to the theoretical structure to achieve agreement appear to be well outside the errors in the correction process. Microwave spectral studies with the 3-^{13}C isotope of propadienone suggest that the heavy-atom chain is not exactly linear but is curved in the plane of the methylene group.[2j] We find no evidence in any of our calculations for a distortion of this type in the equilibrium structure although our calculated vibrational frequencies (see below) do reveal low-energy in-plane vibrational modes. The distinction between our theoretical prediction of a C_{2v} *equilibrium* structure for propadienone and experimental indications[2j,h] of a C_s *vibrational ground-state* structure may be compared with the situation for the molecule $H\text{-}C{\equiv}N^+\text{-}O^-$. Here, the theoretical equilibrium structure is linear[22] whereas the experimentally determined structure for the vibrational ground-state is bent.[23] A recent analysis has demonstratd the compatibility of these seemingly conflicting results.[23]

In contrast to the situation for propadienone (**1**), the structures of propynal (**2**) and cyclopropenone (**3**) are well behaved and the 6-31G** calculated structural parameters are in reasonable agreement with experimental values.[24,25] The only unexpected feature is the C_2–C_3 length in **3** which is overestimated at the 6-31G** (and also 4-31G) level. Multiple bonds, as demonstrated by the results in Table I for acetylene, ethylene, allene, carbon dioxide, formaldehyde, and ketene, are normally underestimated at the Hartree–Fock limit. An STO-3G optimization of cyclopropenone has been reported previously.[26]

Vibrational Frequencies. Vibrational frequencies for the stable H_2C_3O isomers **1**–**3** and for the transition state **4** are displayed in Table II. Two sets of theoretical values are presented, first, the directly calculated harmonic frequencies, and second, values scaled by a factor of 0.9 as an empirical correction to the harmonic approximation. Such a correction procedure has been found[27] to give very reasonable agreement between theoretical and experimental frequencies. For the present set of molecules, such a comparison is only available for propynal. The differences between theory and experiment for some of the frequencies for this molecule are considerably larger than normally observed, and we are not able to account for this discrepancy.

A striking feature of the results for propadienone is the existence of some very low-frequency vibrations. In particular, we note the chain-wagging vibration ν_{12} and the chain-bending vibration ν_8. It may well be that these low-frequency vibrations are responsible for the difficulties in interpreting the microwave spectrum of propadienone and for the apparent disagreement between other theoretically calculated and experimentally derived quantities.

Relative Energies of H_2C_3O Isomers. The data in Table IV show that the relative energies of propadienone and propynal are not very sensitive to improvements in the level of theory. On the other hand, as expected on the basis of previous comparisons[28] of cyclic anc acyclic systems, polarization functions are required to describe adequately the relative energy of cyclopropenone. Electron correlation has only a small effect on the relative energies of **1**, **2**, and **3**. Included in Table IV are relative energies estimated by assuming that electron correlation at the DZd and TZdp levels are the same. Although this assumption that basis set enhancement and correlation effects are additive is clearly only an approximation, the relative energies estimated in this manner are probably more accurate than the other values in the table which correspond to completely neglecting either the correlation or basis set enhancement effect. On this basis, we predict that propynal lies 2.9 kcal mol^{-1} lower and cyclopropenone 3.2 kcal mol^{-1} higher than propadienone. Our overall conclusion is that **1**, **2**, and **3** lie relatively close in energy but in the order propynal < propadienone < cyclopropenone. We believe that the uncertainties in our relative energies (1–2 kcal mol^{-1}) are sufficiently small that this qualitative ordering would be maintained in a more sophisticated treatment.

Decomposition of Propadienone. We have investigated in detail the decomposition of propadienone to vinylidene and carbon monoxide.

$$H_2C{=}C{=}C{=}O \rightarrow H_2C{=}C{:} + CO \tag{1}$$

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(22) (a) McLean, A. D.; Loew, G. H.; Berkowitz, D. S. *J. Mol. Spectrosc.* **1977**, *64*, 184. (b) Poppinger, D.; Radom, L.; Pople, J. A. *J. Chem.* Soc. **1977**, *99*, 7806.

(23) Bunker, P. R.; Landsberg, B. M.; Winnewisser, B. P. *J. Mol. Spectrosc.* **1979**, *74*, 9.

(24) Costain, C. C.; Morton, J. R. *J. Chem. Phys.* 1959, *31*, 389.

(25) Benson, R. C.; Flygare, W. H.; Oda, M.; Breslow, R. *J. Am. Chem. Soc.* **1973**, *95*, 2772.

(26) Fitzpatrick, N. J.; Fanning, M. O. *J. Mol. Struct.* **1975**, *25*, 197.

(27) (a) Komornicki, A., unpublished data. (b) Dr. Warren Hehre (personal communication) has made a similar observation.

(28) See, for example, Lathan, W. A.; Radom, L.; Hariharan, P. C.; Hehre, W. J.; Pople, J. A. *Top. Curr. Chem.* **1973**, *40*, 1.

Table III. Calculated Total Energies (Hartrees)

molecule	4-31G[a]	6-31G**[b]	TZdp[c]	DZd[a]	SCEP/DZd[a]
propadienone	−189.25541	−189.54073	−189.60069[b]	−189.56606	−190.04708
propynal	−189.26255	−189.54552	−189.60645[b]	−189.57331	−190.05308
cyclopropenone	−189.23352	−189.53881	−189.59580[b]	−189.56491	−190.04586
transition structure	−189.19597	−189.49457	−189.55362[b]	−189.52266	−189.99567
vinylidene	−76.65171	−76.76736	−76.79106	−76.77363	−77.00323
acetylene	−76.71141	−76.82186	−76.84837	−76.82812	−77.06824
carbon monoxide	−112.55236	−112.73788	−112.77646	−112.75938	−113.03088

[a] Using 4-31G optimized structures. [b] Using 6-31G** optimized structures. [c] Using TZdp optimized structures unless otherwise noted.

Table IV. Calculated Relative Energies[a] (kcal mol^{-1})

molecule	4-31G	6-31G**	TZdp	DZd	SCEP/ DZd	est[b]
propadienone (**1**)	0	0	0	0	0	0
transition structure (**4**)	37.3	29.0	29.5	27.2	32.3	34.6
propynal (**2**)	−4.5	−3.0	−3.6	−4.5	−3.8	−2.9
cyclopropenone (**3**)	13.7	1.2	3.1	0.7	0.8	3.2
H_2CC: + CO	32.2	22.3	20.8	20.7	(8.1)[c]	
HCCH + CO	−5.2	−11.9	−15.1	−13.5	(−32.7)[c]	

[a] Calculated using total energies of Table II. [b] Values are given which represent a best estimate for the true relative energies assuming additivity of correlation and basis set enhancement effects (see text). [c] Relative energies based on independent molecule calculations on CO, HCCH, and H_2CC.

Table V. Theoretical and Experimental Dipole Moments (D)

molecule	4-31G	6-31G**	DZd	SCEP/ DZd	est[a]	exptl[b]
formaldehyde	3.02	2.66	2.95	2.60	2.31	2.34
ketene	2.21	1.63	1.82	1.54	1.35	1.41
propadienone	3.83	3.12	3.49	3.11	2.74	2.28[c]
propynal	3.51	3.08	3.33	3.06	2.81	2.74[d]
cyclopropenone	5.05	4.69	4.90	4.55	4.34	4.39[e]

[a] Value obtained assuming additivity of correlation and basis set enhancement effects (see text). [b] Unless otherwise noted, from ref 3. [c] Reference 2k. [d] Reference 32. [e] Reference 33.

The transition structure (**4**) for this process, with a long C_2–C_1 bond (Table I), resembles a loose complex of vinylidene and CO. The relative energy of **4** does not show wide variation at the different theoretical levels. Our best estimate of the activation energy for (1) is 34.6 kcal mol^{-1} before correction for zero-point vibrational energy or 32.2 kcal mol^{-1} after correction (cf. Table II). Reaction 1 is endothermic, and thus propadienone is both thermodynamically and kinetically stable with respect to vinylidene and carbon monoxide.

The rearrangement of vinylidene to acetylene

$$H_2C{=}C{:} \rightarrow HCCH \qquad (2)$$

has been shown[29] to require relatively little (8.6 kcal mol^{-1}) activation energy so that the dissociation could be expected, in practice, to be accompanied by rearrangement

$$H_2C{=}C{=}C{=}O \rightarrow HCCH + CO \qquad (3)$$

Reaction 3 is predicted to be exothermic confirming earlier predictions[3] that propadienone is kinetically stable with respect to dissociation and rearrangement to acetylene and carbon monoxide but is thermodynamically less stable than these products. These findings are in turn consistent with the experimental observation[2] of propadienone and its subsequent fragmentation to HCCH + CO.

The sum of independent SCEP energies for vinylidene and CO or acetylene and CO (Table IV) necessarily includes some size-consistency error. The sizeable difference between these values and SCF values in the direction of lowering the relative energies of the dissociated products at least suggests that a true determination of the correlation effects would not lead to a raising of these relative energies.

An interestig result of the SCEP calculations is that correlation actually raises the dissociation barrier by about 5 kcal mol^{-1}. While this may not be surprising, it is not typical since correlation effects are often expected to be larger for a transition structure than for equilibrium structures where SCF wave functions consistently provide good descriptions. Examination of the electron density redistribution due to electron correlation is accomplished with the density difference (SCEP less SCF) plots in Figure 1. These are given for equilibrium propadienone (Figure 1a), the transition structure (Figure 1b), and vinylidene (Figure 1c). In studying the unimolecular rearrangement of H_2N_2,[31] it was found that a qualitative change in the correlation redistribution in electron density through the rearrangement pathway coincided with a lowering of the relative energy of the transition structure. This does not seem to be happening for propadienone. All three plots show similar correlation redistribution around the H_2C_2 fragment, with the transition structure appearing especially like vinylidene. Consistent with the long CO–vinylidene distance in the transition structure, it seems that the electronic structures of the CO molecule and vinylidene have not been strongly perturbed at this point on the reaction profile. The effect of correlation on Mulliken populations is found to be small, but there is an adjustment in the carbon and oxygen net charges of the CO group making it resemble isolated CO even a bit more. Correlation is thus not able to produce a relatively stabilizing redistribution of the electron density.

Dipole Moments. The alternating magnitudes of the dipole moments

$$\mu(H_2CO) > \mu(H_2CCO) < \mu(H_2CCCO) \qquad (4)$$

have been noted previously[3] and are reproduced by the calculations presented here (Table V). However, whereas all levels of theory predict that $\mu(H_2CCCO) > \mu(H_2CO)$, the experimental values are in the reverse order. There is no immediate explanation for this discrepancy although it is likely to be connected with differences between the theoretically predicted C_{2v} equilibrium structure and the experimentally determined C_s structure for the ground vibrational state of propadienone. Indeed, very recent results[2k] have indicated that the originally reported[2f] moment of 2.14 D corresponds to the μ_a component and that there is, in addition, a μ_b component of 0.80 D leading to a resultant moment of 2.28 D.

For the remaining molecules in Table V, the directly calculated dipole moments are somewhat higher than experimental values. Included also in Table V are estimated values obtained by assuming that the effect of correlation on the dipole moment is the same at the DZd and 6-31G** levels. Again, this is only an approximation, but the resultant moments (excluding of course the structurally questionable propadienone) are in remarkable agreement with experiment with a mean absolute error of 0.05 D. Our calculations strongly support a redetermined value of the

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dipole moment of propynal (2.74 D^{32} compared with the previous value of 2.46 D^{33}).

Conclusions

Several important points emerge from this study.

(1) Propadienone, propynal, and cyclopropenone have comparable energies but in the order propynal < propadienone < cyclopropenone.

(2) Propadienone is predicted (6-31G**) to have an equilibrium structure which is planar with C_{2v} symmetry but to possess low-frequency vibrations of b_1 and b_2 symmetry which allow easy distortion from such a structure. This may be responsible for the apparent disagreement between theoretically calculated and experimentally observed properties (e.g., rotational constants, dipole moment) for propadienone.

(3) Propadienone can dissociate to vinylidene plus carbon monoxide via a transition state resembling a weak complex of the products in an endothermic reaction requiring about 32 kcal mol^{-1} activation energy. Subsequent rearrangement of vinylidene to acetylene leads to an exothermic dissociation plus rearrangement reaction.

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Hexaammineruthenium(II,III) and Pentaamminedinitrogenruthenium(II). A Hartree-Fock-Slater Study

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Abstract: Discrete variation method Hartree-Fock-Slater studies are reported for the title compounds. The significant σ covalency and strong π back-bonding in the dinitrogen complex are apparent from populations, energy shifts, optical spectra, and reorganization effects on optical excitation; the energy levels are strongly perturbed by the strong covalency from their pseudooctahedral crystal field values. Transition-state calculations yield optical and photoemission results in good agreement with experiments. In the dinitrogen compound, the directly bonded N is considerably more negative, in agreement with simple electrostatic and bonding arguments.

The rich redox chemistry of Ru^{II} and Ru^{III} complexes has been carefully elucidated, particularly in the early probing and elegant work of Taube and his students.[1-3] In particular, the strong π-back-bonding ability of Ru has been demonstrated in a series of chemical and physical studies. One of the most striking evidences of the π-base strength of Ru is the easy preparation and marked stability of the $(NH_3)_5Ru^{II}(N_2)$ (I) complex, which was one[4] of the first stable dinitrogen metal complexes to be prepared; the N_2 ligand will[5] actually displace water from the aquopentaamineruthenium(II). The properties of I have been widely interpreted[3] as arising from the strength of its π back-bonding. Comparison with the $(NH_3)_6Ru^{II}$ (II) complex, which contains the same primary coordination sphere but cannot support π back-donation, should be particularly helpful in clarifying the role of this interaction. More recently, attention has been focused[6-13] on the intramolecular electron-transfer properties of binuclear complexes containing the $(NH_3)_5Ru^{II}$ L species, where L is a π-acceptor ligand (N_2, pyrazine, 4,4′-bipyridyl, cyanogen, etc.).

Table I. Internuclear Distances (μ_β)[a]

II $Ru(NH_3)_6{}^{2+}$		I $(NH_3)_5RuN_2{}^{2+}$		III $Ru(NH_3)_6{}^{3+}$	
Ru-N	4.052	Ru-N(eq)	4.014	Ru-N	3.976
N-H	1.907	Ru-N(ax)	4.044	N-H	1.907
H-H	3.048	Ru-N	3.645	H-H	3.048
		N-N	1.124		
		N-H	1.907		
		H-H	3.048		

[a] Taken from ref 26 and 21. The Ru-N-N group is from the dimer and probably overstates the Ru-N distance; see text.

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