S. Kato, S. Yamabe, and K. Fukui, *ibid.*, **60**, 572 (1974).
(18) C. A. Coulson and H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A*, **192**, 16 (1947).
(19) H. Fujimoto, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **43**, 2936 (1971).
(20) On the importance of excited electron configurations in unimolecular reactions, see the works by Bader, Salem, and Pearson (R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962); L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); R. Pearson, *J. Am. Chem. Soc.*, **91**, 1252, 4947 (1969)).
(21) R. S. Mulliken, *J. Chim. Phys. Phys.-Chim. Biol.*, **46**, 497 (1949).
(22) A determinantal wave function Ψ_p is given by $|\Phi_p \cdot \bar{\Phi}_p|$ where Φ_p and $\bar{\Phi}_p$ represent collectively the spin orbitals of isolated reactants with spin α and spin β, respectively, appearing in the wave function Ψ_p. Similarly, we have $\Psi_q = |\Phi_q \cdot \bar{\Phi}_q|$. Then, the overlap integral $S_{p,q}$ is given by

$$S_{p,q} = |s_{p,q}| \cdot |\bar{s}_{p,q}|$$

where

$$s_{p,q} = \int {}^{\dagger}\Phi_p \Phi_q d\tau \text{ and } \bar{s}_{p,q} = \int {}^{\dagger}\bar{\Phi}_p \bar{\Phi}_q d\tau$$

The MO's of reactants are presented in the LCAO forms

$$\Phi_p = c_p\chi,\ \bar{\Phi}_p = \bar{c}_p\bar{\chi},\ \Phi_q = c_q\chi, \text{ and } \bar{\Phi}_q = \bar{c}_q\bar{\chi}$$

By the use of the inverse of the overlap matrices $s_{p,q}$ and $\bar{s}_{p,q}$, the bond order matrices are defined by

$$P_{p,q} = c_q s_{p,q}{}^{-1\dagger} c_p \text{ and } \bar{P}_{p,q} = \bar{c}_q \bar{s}_{p,q}{}^{-1\dagger} \bar{c}_p$$

Now it is easy to calculate the integral $H_{p,q}$ weighted by the normalizing factors due to the MO overlaps by means of the transformed bond orders, in a similar way as the computation of the total electronic energy in the SCF MO theory with orthonormal one-electron functions (H. Fujimoto and N. Kosugi, *Bull. Chem. Soc. Jpn.*, **50**, 2209 (1977)).
(23) A. Dedieu and A. Veillard, *J. Am. Chem. Soc.*, **94**, 6730 (1972). The geometry obtained by Dedieu and Veillard may be somewhat arbitrary.
(24) Orbital constants were taken after Stewart et al. See R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970); W. J. Hehre, R. F. Stewart, and J. A. Pople, *ibid.*, **51**, 2657 (1969).
(25) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **42**, 3399 (1969).
(26) S. Winstein and R. B. Henderson, "Heterocyclic Compounds", Vol. 1, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1950, p 22.
(27) On the effect of dipolar fields on chemical interactions, see S. Yamabe, S. Kato, H. Fujimoto, and K. Fukui, *Theor. Chim. Acta*, **30**, 327 (1973).
(28) This assumption is obviously based on a very crude approximation. Since the changes in nucleus-electron attraction and electron-electron repulsion with the change in the interatomic distance are different, the right-hand side of eq 3 does not necessarily vanish even when the reagent B is neutral and nonpolar.
(29) One may notice that locally excited configurations participate in the accumulation of electron density in the intermolecular region and, hence, in the formation of chemical bonds between reagent and reactant through the interaction with electron-transferred configurations. The significance of such orbital interactions was discussed recently. See S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **97**, 6108 (1975).
(30) P. Cremaschi and M. Simonetta, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1901 (1974).
(31) R. E. Townshend, G. Ramunni, G. Segal, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **98**, 2190 (1976).
(32) L. A. Burke, G. Leroy, and M. Sanna, *Theor. Chim. Acta*, **40**, 313 (1975).
(33) L. Salem, *Chem. Br.*, **5**, 449 (1969).
(34) The transition state obtained by Leroy et al. is more reactant-like. See ref 32.
(35) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 6225 (1974).
(36) The symbol π is used to specify the MO's of norbornadiene, although the conjugation is not pure π type.
(37) M. V. Basilevsky and I. E. Chelenov, *Theor. Chim. Acta*, **15**, 174 (1969).
(38) J. R. Hoyland, *Theor. Chim. Acta*, **22**, 229 (1971).
(39) H. Fujimoto, S. Yamabe, T. Minato, and K. Fukui, *J. Am. Chem. Soc.*, **94**, 9205 (1972).
(40) Within the framework of the simple Hückel MO approximation, we have

$$c_\alpha{}^j = c_\beta{}^i \text{ and } c_\beta{}^j = -c_\alpha{}^i$$

Then, the changes in atomic densities and bond order are given by

$$\Delta q_\alpha = 2c_\alpha{}^i c_\beta{}^i,\ \Delta q_\beta = -\Delta q_\alpha$$

$$\Delta p_{\alpha\beta} = 2\{-(c_\alpha{}^i)^2 + (c_\beta{}^i)^2\}$$

From the normalization of the MO ϕ_i, i.e., $(c_\alpha{}^i)^2 + (c_\beta{}^i)^2 = 1$, we immediately arrive at the conclusion

$$\left.\begin{array}{l} |\Delta q|: \text{maximum} \\ |\Delta p|: \text{minimum} \end{array}\right. \quad \text{when } c_\alpha{}^i = c_\beta{}^i$$

and

$$\begin{array}{lll} |\Delta q|: \text{minimum} & \text{when,} & c_\alpha{}^i = \pm 1 \text{ and } c_\beta{}^i = 0 \\ |\Delta p|: \text{maximum} & \text{or} & c_\alpha{}^i = 0 \text{ and } c_\beta{}^i = \pm 1 \end{array}$$

(41) In the case of the bimolecular nucleophilic substitution reaction mentioned above, we obtain $C_{i \rightarrow l}{}^2 \sim 0.040$ and $C_0 C_{k \rightarrow l} \sim -0.057$ where the MO's i, k, and l correspond to the $2p_x$ of fluoride ion and $5a_1$ and $6a_1$ MO's of methyl fluoride, respectively. A similar relation also holds in the nonpolar reaction between methylene and hydrogen.
(42) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).

Gaseous Ions. 4. MINDO/3 Calculations for Some Simple Organic Cations and for Their Hydrogen Elimination Reactions

Michael J. S. Dewar* and Henry S. Rzepa

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received November 2, 1976*

Abstract: The structures and relative energies of $CH_4{}^{+}\cdot$, $C_2H_6{}^{+}\cdot$, and the classical and nonclassical forms of the ethyl and vinyl cations are reported. The results are in agreement with recent ab initio calculations in predicting a structure of C_{2v} symmetry for $CH_4{}^{+}\cdot$ and bridging structures for the ethyl and vinyl carbonium ions. The calculated activation energies for the elimination of hydrogen from these and other small cations agree with experimental estimates. The structures of the transition states for the formally forbidden 1,2-eliminations were found to be concerted but not synchronous, and to differ significantly from the transition state for the allowed 1,1-elimination of hydrogen from $C_2H_5{}^{+}$. The calculated frequencies of the imaginary modes for the transition states appear to be related to the observed energy distribution in the products.

Previous papers[1-3] of this series have reported a detailed MINDO/3[4] study of the $C_7H_7{}^{+}$ and $C_7H_8{}^{+}$ systems, and of the effects of various substituents on the interconversion of benzyl cation and tropylium. The results were in satisfactory agreement with the very detailed experimental evidence currently available for these systems, suggesting that MINDO/3 should prove generally useful for investigating the properties of organic ions in the gas phase. Studies[5,6] of various simple organic cations, both "classical" and "nonclassical", have, moreover, given satisfactory results, comparable with those from the rather detailed ab initio calculations of Pople et al.[7] Here we report MINDO/3 studies of two of the simplest organic cations, $CH_4{}^{+}$ and $C_2H_6{}^{+}$, and of a number of reactions involving a formal 1,2-elimination of hydrogen (H_2) from various cations. The heats of formation of $CH_4{}^{+}$ and $C_2H_6{}^{+}$ have, of course, been determined very precisely by photoelec-

Table I. The Relative Energies of the Isomers of $CH_4^{+\cdot}$, $C_2H_6^{+\cdot}$, and $C_2H_4^{+\cdot}$

		ΔH_f(calcd),[a]	ΔH_f(obsd),[b]		Rel energies		
	Point group	kcal mol^{-1}	kcal mol^{-1}		M/3	4-31G[c]	6-31G*[c]
$CH_4^{+\cdot}$	D_{2d} (**4**)	268.9		2[d]	5.0	−2.0	>0
	C_{2v} (**5**)	263.9	274	0	0.0	0.0	0.0
	C_{3v} (**6**)	279.8		2	15.9	1.1	>0
$C_2H_6^{+\cdot}$	D_{3d} (**3**)	247.3		2	15.9		
	C_s (**1**)	231.4	245	0	0.0		
	C_{2h} (**2**)	236.5		3	5.1		
$C_2H_4^{+\cdot}$	D_2 (**7**)	243.3	253	0	0.0		
	C_1 (**8**)	252.5		0	9.2		

[a] Calculated using the half-electron method. [b] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", NSRDS-NBS 26, Washington, D.C., 1969. [c] Reference 7. [d] Number of negative eigenvalues on diagonalizing the force constant matrix.

tron spectroscopy but their structures have not been established experimentally. The 1,2-elimination of hydrogen from organic cations is an interesting reaction which has recently been studied in detail by Williams and Hvistendahl.[8,9] They found that such reactions fall into two distinct groups, depending on whether the excess energy appears as kinetic energy, or as internal (vibrational) energy, in the products.

Procedure

The calculations were carried out using the standard MINDO/3[4] program, geometries being found by minimizing the energy with respect to all geometric variables using the standard DFP method. Transition states were located either by the normal reaction path method or by a two-dimensional grid search, which involved fixing two variables and minimizing the energy with respect to the rest. This was found necessary in studying the elimination of hydrogen, where the H-H bond length and the length of the breaking X-H bond were taken as the fixed coordinates. Stationary points were located by inspecting the scalar gradients of the two fixed geometric variables according to the McIver-Komornicki criterion.[10] These points were refined by minimizing the squares of *all* the scalar gradients[10] and they were characterized as saddle points by calculating[11] the force constant matrix and establishing that it had only one negative eigenvalue,[10] the associated eigenvector corresponding to the motion along the reaction coordinate.

The calculations for open-shell species were carried out using an unrestricted version[12,13] of MINDO/3 (UMINDO), the geometries of stable species and transition states being found by procedures similar to those for closed-shell systems. The geometries were then reoptimized using the "half-electron" (h-e) method,[14] the geometries and energies quoted here being the h-e values. Extensive tests[4,14] have shown that h-e gives good values for the energies of open-shell systems, while those from UMINDO are more negative by 2-8 kcal/mol. On the other hand, MINDO/3 (h-e) requires far more time for geometry optimizations, owing to problems that arise in the calculation of derivatives of the energy. Since UMINDO gives geometries that are very close to the h-e ones, the most efficient procedure is to carry out the h-e geometry optimization starting with the geometry given by UMINDO.

In one connection, we needed to estimate vibrational energies of certain species. These were found from calculated (MINDO/3 or UMINDO) vibrational frequencies.[11,15]

The $C_2H_6^{+\cdot}/C_2H_4^{+\cdot}$ System. There has long been controversy concerning the equilibrium structures of the molecular ions of ethane and methane.[7,18] Removal of an electron from the degenerate t_2 orbital of methane or the e_g orbital of ethane should lead to Jahn-Teller-type distortions of the geometries, whereas ionization from the a_{1g} orbital of ethane should lead to no such distortion. Two possible distortions which remove the orbital degeneracy in ethane lead to C_2 (**1**) and C_{2h} (**2**) structures, while an undistorted A_{1g} state of D_{3d} symmetry is also possible (**3**). There are similarly three possible ways of removing the orbital degeneracy in $CH_4^{+\cdot}$, leading to structures of D_{2d} (**4**), C_{2v} (**5**), and C_{3v} (**6**) symmetry. As a prelude to a study of the fragmentation of ionized ethane, we have calculated the relative energies of all these isomers. These are compared in Table I with the ab initio results of Pople.[7]

Only one stable minimum, corresponding to a force constant (Hessian) matrix with no negative eigenvalues, was found for each species, viz., **1** and **5**. This agrees with the most recent ab initio studies[7] where corrections for electron correlation were found necessary. For ethane, this result seems in agreement with the available evidence,[18a] which suggests that the ground ionic state is Jahn-Teller distorted, although further differentiation between **1** and **2** was not possible.

The ground state of $C_2H_4^{+\cdot}$ was found to correspond to ionization from the b_{1u} orbital and was of D_2 symmetry (**7**), the C-C bond being twisted by 44°. Although Pople et al.[16] calculated this ion to be planar, it is probably twisted to some degree.[17] An unexpected isomer (**8**) was also located, 12.6 kcal/mol higher in energy than **7**. The energy of the transition state **9** corresponded to a barrier for the conversion **8** → **7** of 3.4 kcal/mol. The structures and energies of the species **1-9** are shown in Figure 1.

The good results for these nonclassical species encouraged us to investigate the fragmentation reaction reported by Hvistendahl and Williams;[8,9] i.e.

$$C_2H_6^{+\cdot} \rightarrow C_2H_4^{+\cdot} + H_2 \qquad (1)$$

Measurements of the appearance potential for the metastable peak corresponding to eq 1 provided an estimate of the activation energy (13 kcal/mol). The broadening of this metastable peak suggested that the products were being formed with 4.4 kcal/mol of kinetic energy.

A grid search (see above) located a stationary point corresponding to **10** which was refined and characterized.[10,11] The structure is shown in Figure 2, together with an illustration of the relative motions of the atoms along the transition vector. These correctly correspond to loss of molecular hydrogen. The calculated activation energy is 16.8 kcal/mol for the forward reaction and 4.9 kcal/mol for the reverse reaction, which compares very favorably with the values (13, 4.5 kcal/mol) reported by Hvistendahl and Williams.[8,9]

The structure of **10** is interesting. The transition state is very unsymmetrical, one C-H bond being almost broken (1.55 Å) and the other much less so (1.24 Å), while the H-H bond is incompletely formed. The reaction is therefore concerted but not synchronous, the transition state corresponding closely to a derivative of the CH_5^+ cation.[5] Inspection of the HOMO confirms this, the unpaired electron residing mainly in a *p* orbital on C_1 (Figure 2), corresponding to $CH_2^{\cdot}$-CH_4^+. Thus although **10** (Figure 2) corresponds to the transition state of a concerted 1,2-elimination, it has certain unusual features

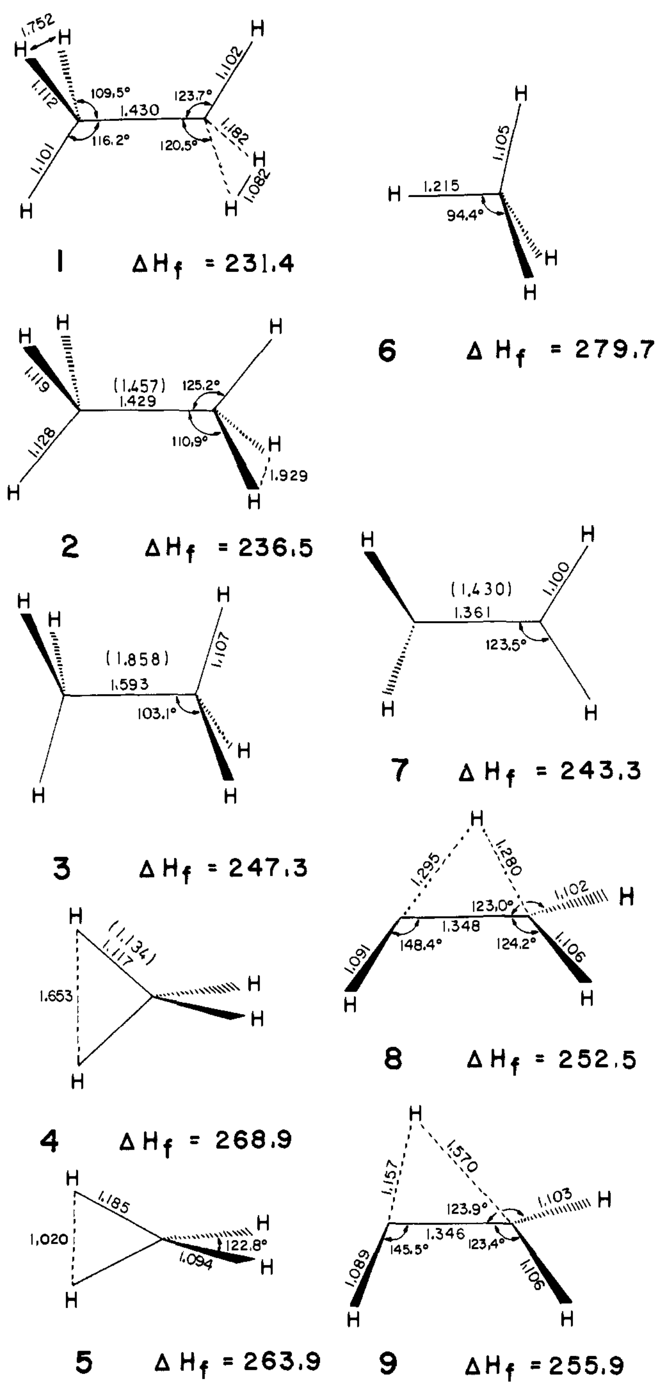


Figure 1. Calculated heats of formation (in kcal/mol) and geometries (bond lengths in Å) for the $C_2H_6^{+}\cdot/C_2H_4^{+}\cdot$ system. Bond lengths in parentheses are the STO-3G values quoted in ref 7b.

which were not previously suspected.

An obvious alternative pathway for elimination of hydrogen from **1** is dissociation of the σ-bonded H_2 moiety. We studied this by using one of the CH bond lengths as the reaction coordinate. A continuous pathway with no reverse activation energy was found. The product, however, was **8**, not **7**. Subsequent conversion of **8** to **7** requires a further 3.4 kcal of energy (vide supra), which means that the activation energy for 1,1-elimination of hydrogen is 24.5 kcal/mol, or 7.7 kcal/mol more than for the concerted 1,2-elimination. This is in agreement with the observation that only HD is lost from $CD_3CH_3^{+}\cdot$.[8,9]

Hvistendahl and Williams[8,9] also studied the elimination of hydrogen from **7**, with the rather curious conclusion that the measured appearance potential corresponds to an activation energy *less* than the known endothermicity of the reaction. It therefore seems certain that the reverse activation energy (if any) must be small. We calculated the addition of hydrogen to ionized acetylene, following a pathway corresponding to 1,1-addition, and found no activation energy for formation of **7**. The calculated heat of reaction was 54.4 kcal/mol, compared with a value of 64 kcal/mol quoted by Hvistendahl and Williams.[9] This result, however, is inconsistent with the observation of large deuterium isotope effects for the reaction.[8c]

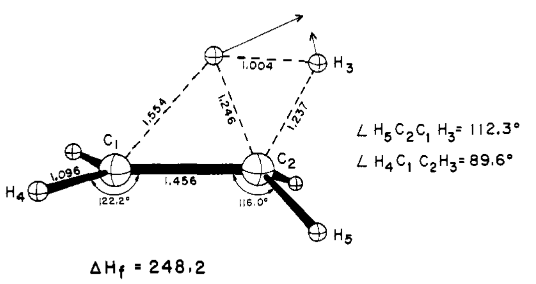


Figure 2. ORTEP plot of the transition state **10** for the elimination of molecular hydrogen from $C_2H_6^{+}\cdot$ (bond lengths in Å). The arrows illustrate the form of the normal mode corresponding to the reaction coordinate (see also Figures 4, 6, 8, and 10).

Table II. The Relative Energies of the Vinyl and Ethyl Carbonium Ions

	ΔH_f(calcd), kcal mol^{-1}	ΔH_f(obsd), kcal mol^{-1}	Rel energies, kcal/mol M/3	4-31G	6-31G*/UMP2[a]
C_2H_3 (**11**)	248.3	266[b]	0	0	0
(**14**)	253.6		5.3	−19.2	3.9
C_2H_5 (**11**)	205.7	219[c]	0	0	0
(**12**)	214.7		8.0	−7.3	6.3

[a] Reference 7. [b] F. P. Lossing, *Can. J. Chem.*, **49,** 357 (1971). [c] Footnote *b* Table I.

The $C_2H_5^+/C_2H_3^+$ System. Much computational time and effort has been expanded on studies of the relative stabilities of the nonclassical and classical forms of the ethyl (**11, 12**) and vinyl (**13, 14**) cations. Pople[7] has summarized the most recent investigations, and Weber and McLean[19] and Zurawski, Ahlrichs, and Kutzelnigg[20] have contributed further discussion. The Roothaan-Hall calculations appear to be in agreement that the isomers **11** and **13** are as stable as, or more stable than, the "classical" ions **12** and **14.** Table II gives the MINDO/3 heats of formation of these ions, and compares the relative energies with those quoted by Pople.[7] As appears to be the case for all positive ions, MINDO/3 predicts the heats of formation to be too low by about 10–12 kcal/mol. The relative energies of the two isomeric forms agree very well with the predictions of Pople[7] and of Zurawski, Ahlrichs, and Kutzelnigg,[20] using large basis sets with polarization functions and corrections for electron correlation.

Recently Weber and McLean[19] have reported calculations for **13** and **14,** using a basis set "of double-ζ plus polarization quality", with and without CI. Including CI, they found **13** and **14** to be equal in energy, with the transition state **15** 1.6 kcal/mol higher. The MINDO/3 value for the barrier is 0.02 kcal/mol. Their calculation was, however, based on the assumption that inclusion of CI would not alter the geometries, these being taken from the single-conformation results. This procedure may be acceptable for "normal" molecules with localized bonds but may not be valid for nonclassical structures. Their failure to optimize the geometry of **13** with CI therefore weakens their conclusions. One might add that since calculations of this kind are known to be very sensitive to the choice

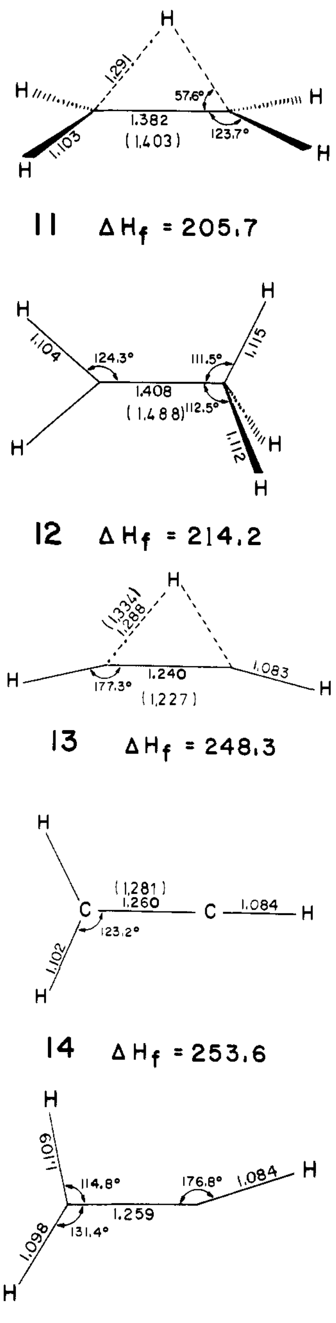


Figure 3. Calculated heats of formation and geometries for the $C_2H_5^+$/$C_2H_3^+$ system.

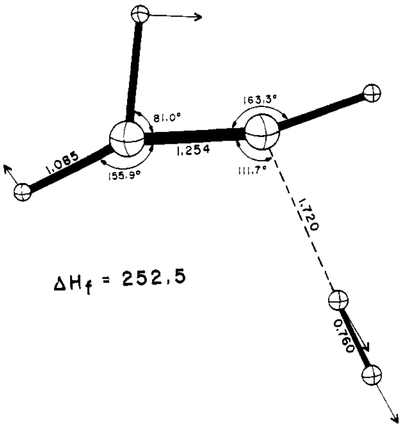
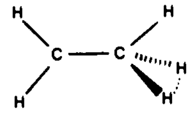


Figure 4. ORTEP plot of the transition state **17** for the elimination of molecular hydrogen from $C_2H_5^+$.



16

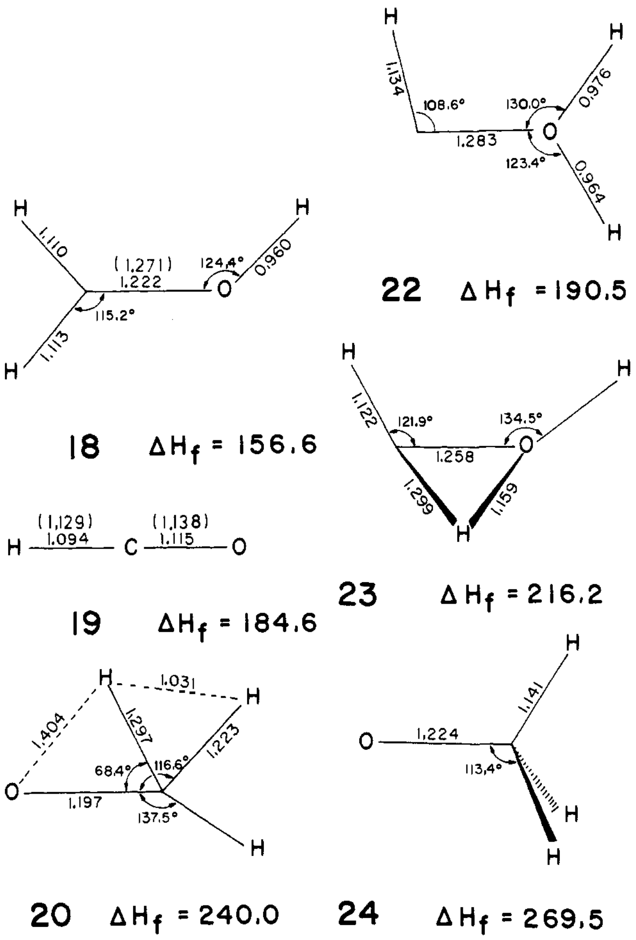
of basis set, the results are more convincing if carried out with a basis set which has been tested in this connection, in this case by calculations for nonclassical structures whose properties are known with reasonable assurance (CH_5^+, B_2H_6, etc.). Weber and McLean give no indication that this was the case for the unspecified basis set they used.

Loss of hydrogen from ethyl cation is thought to proceed by 1,1-elimination,[8,9] activation energies of 67[8,9] and 55 kcal/mol[21] having been reported for this reaction. We initially carried out a grid search using the C-H and H-H distances as reaction coordinates and keeping the two breaking C-H distances equal. A stationary point was located, with a structure corresponding to **16**, but the force constant matrix had two negative eigenvalues, the smaller corresponding to the antisymmetric combination of the two C-H stretches. On displacing the geometry slightly along the latter coordinate, a stationary point of lower energy was located, with a geometry corresponding to **17** and with only one negative force constant. The transition vector corresponded to loss of hydrogen (Figure 4). The calculated activation was 47 kcal/mol, in moderate agreement with the value of 55 kcal/mol reported by Vestal,[21] but less so with the result of Hvistendahl and Williams[8,9] (67 kcal/mol).

The geometry of the transition state is again unexpected, one C-H bond being completely broken and the other almost completely so. This is certainly in accord with McIver's postulate,[22] that a symmetric transition state is likely to be unstable with respect to an antisymmetric distortion, but not with the classically accepted formalism for a 1,1-elimination. There remains nevertheless a significant distinction between the two transition states **10** and **17**, particularly in the form of the transition vector. We will return to this point later.

The CH_2OH^+/CHO^+ System. The equilibrium geometries of $CH_2{=}OH^+$ (**18**) and HCO^+ (**19**) (Figure 5) present no novel features. The MINDO/3 values for the heats of formation of **18** (156.6 kcal/mol) and **19** (184.6 kcal/mol) are both about 12 kcal/mol less than the measured values (167[23] and 199 kcal/mol,[24] respectively). The elimination of molecular hydrogen was studied by constraining the molecule to C_s symmetry and carrying out the usual grid search. A stationary point (**20**) was located, with two negative eigenvalues in the Hessian matrix. The smaller corresponded to an out of plane vibration, and displacement of the coordinates in this direction gave a transition state (**21**) (Figure 6) with the correct transition vector. The heat of formation calculated for **21** corresponds to an activation energy 83.3 kcal/mol in the forward direction and 55.3 kcal/mol in the reverse direction. The corresponding values obtained by Hvistendahl and Williams[8,9] by measurements of appearance potentials were 80 and 53.1 kcal/mol. The MINDO/3 result is clearly in better agreement with experiment than the value (164 kcal/mol) recently calculated by Saebø[25] for the forward reaction, using the R-H method with a basis set of moderate size.

The salient features of the transition state **21** are very similar



18 ΔH_f = 156.6

19 ΔH_f = 184.6

20 ΔH_f = 240.0

22 ΔH_f = 190.5

23 ΔH_f = 216.2

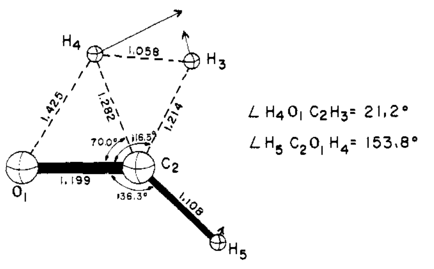
24 ΔH_f = 269.5

Figure 5. Calculated heats of formation and geometries for the CH_3O^+/CHO^+ system.

to those of **10**, the elimination being concerted but not synchronous. The presence of an oxygen atom has not modified the structure of **21** very greatly, although it is interesting to note that the O-H bond length (1.425 Å) is much greater than the C-H bond length (1.214 Å). A comparison with Saebø's[25] results is unfortunately not possible, since he did not report his calculated geometry in detail. However, the MINDO/3 values for the C-O (1.199 Å) and H-H bond lengths (1.058 Å) compare favorably with the ab initio values of 1.191 and 1.070 Å, respectively. Our calculations once again emphasize the need for rigorous optimization of *all* geometric variables, and rigorous characterization of the transition state, in calculations of this kind. Failure to do this can lead to totally spurious geometries (cf. **20** or **16**).

Since a 1,2-elimination must involve an orbital crossing, a single determinantal wave function may not suffice to describe the electronic state of the transition state. We found that in the case of **21**, a (17 × 17) CI treatment,[26] including several singly and doubly excited configurations, did not lower the energy by more than 2 kcal/mol. It is therefore evident that in this case a single determinantal wave function adequately describes the electronic structure of the transition state.

All these reactions take place by a synchronous combination of a 1,2-hydrogen migration and 1,1-elimination of H_2. In the case of **18**, the migration can in principle take place in either direction, from oxygen to carbon or from carbon to oxygen. The calculations reported above corresponded to the former. We next studied the alternative possibility, i.e., migration of hydrogen from carbon to oxygen. To our surprise, this led to a stable carbenoid isomer (**22**) of **18** rather than to elimination of H_2. The calculated heats of formation of singlet and triplet **22** were 190 and 213 kcal/mol, respectively. The corresponding transition state (**23**) had a calculated heat of formation of 216.6 kcal/mol, corresponding to an activation energy of 60 kcal/mol for conversion of **18** to **22**, while the heat of formation calculated for **22** (190.5 kcal/mol) corresponded to a heat of reaction of +34 kcal/mol. Since the activation energy calculated for conversion of **18** to **22** is much less than that for loss of H_2, we would then expect the equilibrium **18** $\rightleftarrows$ **22** to be established, leading to scrambling of the hydrogen atoms in **18**. Such scrambling is, however, not observed. The corresponding dissociation of CH_2O^+D gives only (HD + HCO), no DCO being formed.[27] MINDO/3 therefore seems to be overestimating the stability of the carbene **22** and hence the ease of its formation from **18**.



ΔH_f = 239.9

Figure 6. ORTEP plot of the transition state **21** for the elimination of molecular hydrogen from protonated formaldehyde.

This is not in fact surprising, because both the carbon atom and the oxygen atom in **18** have unshared pairs of electrons in hybrid AOs (in a simple MO description). The INDO approximation, on which MINDO/3 is based, leads to an underestimate of the interelectronic repulsions in such cases as a result of the neglect of one-center differential overlap.[4a] Indeed, the heats of formation of analogous carbenes (CCl_2, CF_2) are also greatly underestimated by MINDO/3.[4a] This problem is avoided in the NDDO approximation and a suitable version of this (MNDO[28]) has recently been developed here. We therefore repeated the calculations for **18** and **22** using MNDO and, of course, optimizing their geometries. The heat of formation calculated for **18** (155.5 kcal/mol) agreed very nicely with the MINDO/3 value but that for **22** (224.4 kcal/mol) was greater by over 30 kcal/mol. While we did not locate the transition state (**23**) for conversion of **18** to **22** by MNDO, it seems likely that it must be close to **22** in structure since the reaction is so very endothermic. If so, the activation energy should also be ca. 30 kcal/mol greater than the MINDO/3 value and so greater than that for loss of H_2 from **18** via **20**.

We also examined the singlet methoxy cation, CH_3O^+. This was found not to be a minimum on the potential surface; the structure (**24**) was calculated by enforcing C_{3v} symmetry. The bond length (Figure 5) is shorter than we find using the STO-3G basis set ($\simeq$1.45 Å). MINDO/3 in general predicts bond lengths for the cations studied here which are shorter than those given by STO-3G calculations[7b] (see figures). For open-shell cations, however, Pople et al.[7b] used an unrestricted procedure, which was found to give significantly longer bond lengths (i.e., by 0.036 Å in the case of $H_2CNH^{+\cdot}$) than a restricted method, analogous to the half-electron method used in our studies. The differences between the MINDO/3 and STO-3G geometries (e.g., $CH_3NH_2^{+\cdot}$, see Figure 7) may be partly due to this.

The $CH_5N^{+\cdot}$/$CH_3N^{+\cdot}$ System. The structures and energies of ionized methylamine (**25**) and other intermediates are shown in Figure 7. The nitrogen center is planar, corresponding to ionization from the lone pair orbital, and the calculated heat of formation (190.4 kcal/mol) is close to the experimental value[29] (201 kcal/mol). By analogy with the carbene **22**, we

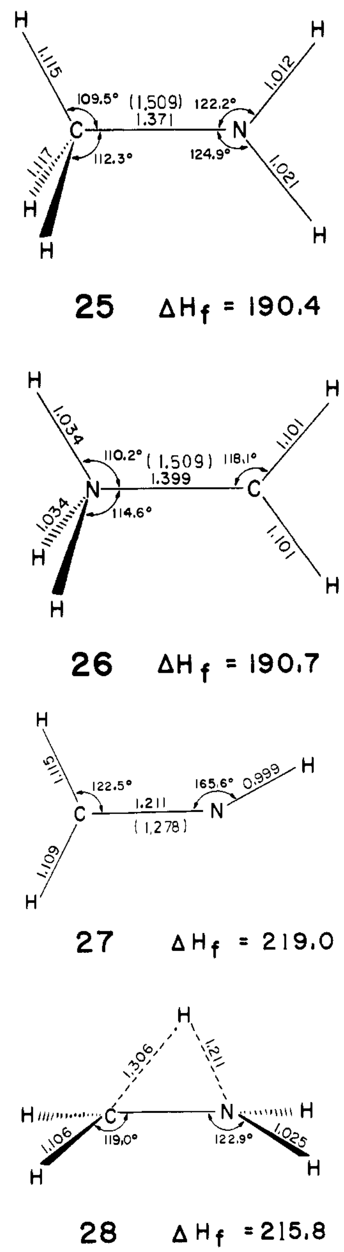


Figure 7. Calculated heats of formation and geometries for the $CH_5N^{+\cdot}/CH_3N^{+\cdot}$ system.

investigated the isomer **26**, and surprisingly found that the energy (190.7 kcal/mol) is only slightly higher than that of **25**. MNDO[28] gives values of 206.1 and 194.2 kcal/mol for **25** and **26**, respectively, and a RH UHF calculation, using the MNDO geometries and the 4-31G basis set,[30] predicted **26** to be more stable by 0.7 kcal/mol. The transition state **28** connecting the two species had an energy of 215.8 kcal/mol, giving a barrier of 25.4 kcal/mol for the hydrogen scrambling process. This low value is not unreasonable, since MINDO/3 correctly predicts bridging species such as **11** to be highly stabilized.

Loss of hydrogen from **25** is calculated to be endothermic by 29 kcal/mol and Hvistendahl and Williams[8] have reported that the products are formed with 19 kcal of translational energy. These values imply an activation energy for **25** → **27** of at least 48 kcal/mol. The transition state **29** was located by the usual method (Figure 8) and was found to have an energy of 271.5 kcal/mol, giving a barrier for the elimination of hydrogen of 81 kcal/mol. This is far in excess of the barrier required for hydrogen scrambling and is not in accord with the observation reported by Hvistendahl and Williams[8] that $CH_3ND_2^{+\cdot}$ eliminates HD specifically. Since the energy of **29** seems rather high, we searched a different part of the potential surface, and located a stationary point corresponding to **30**. The force constant matrix for this species had *five* negative eigenvalues, none of which corresponded to loss of hydrogen, and the energy was about 286 kcal/mol. The discrepancy between the barriers for hydrogen scrambling and hydrogen loss is therefore somewhat puzzling.

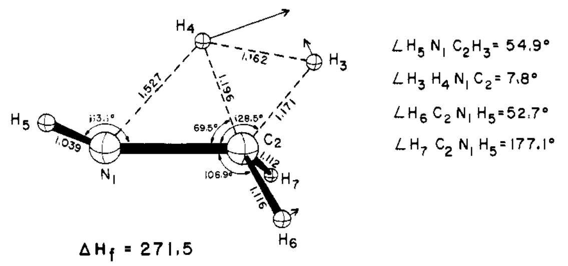
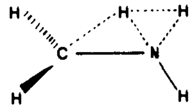
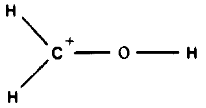


Figure 8. ORTEP plot of the transition state **29** for the elimination of molecular hydrogen from ionized methylamine.



30

The CH_2SH^+/CHS^+ System. A comparison of **18** with the thio analogue **31** is of some interest, in view of recent RH calculations,[31] using the 4-31G basis set. These predict the geometric inversion of **18** to proceed via a linear transition state **32**, but that of **31** to involve a bent transition state of C_s symmetry (**33**), the calculated activation energies being 14 and 36.5 kcal/mol, respectively.



32

Using MINDO/3, we find that **32** does indeed represent the transition state for inversion, with a barrier of 8.3 kcal/mol, in contrast to the sulfur analogue which is bent (Figure 9) with a barrier of 18.3 kcal/mol. The two methods agree qualitatively, the MINDO/3 barriers being somewhat lower than the ab initio values.

We were also able to locate several other minima on the CH_3S surface for which no corresponding oxygen analogue existed. These represented the bridged ions **34** and **35**, whose structures, along with that of the carbene **36**, are shown in Figure 9. These were all higher in energy than **31**, by 13.7, 55.3, and 43.6 kcal/mol, respectively. The transition states for the conversions **31** → **35** and **35** → **36** had activation energies of 56.8 and 56.1 kcal/mol. The former represents the calculated barrier for hydrogen scrambling, compared with 60.0 kcal/mol for the oxygen analogue **24**. Investigation of the alternate pathway **31** → **34** led to a transition state **37**, which is distinguished from **33** by having no symmetry. Opening of the bridging complex in the other direction was studied by the usual grid search. A transition state **38** was located, having one negative eigenvalue corresponding to loss of hydrogen (Figure 10). The activation energy was calculated to be 45.8 kcal/mol. The available experimental evidence[8] suggests that the products from fragmentation of **31** are formed with 20 kcal of translational energy, in comparison with a value of 33 kcal/mol for the products from protonated formaldehyde. The lower calculated activation energy for fragmentation of protonated

Table III. Forward and Reverse Activation Energies ($\Delta H^{\ddagger}$) for Hydrogen Elimination Reactions

Reaction	$\Delta H^{\ddagger}_{calcd}$, kcal/mol	$\Delta H^{\ddagger}_{obsd}$,[a] kcal/mol	$\Delta H^{\ddagger}_{r}$(calcd)[b]	$\Delta H^{\ddagger}_{r}$(obsd)[a,b]	$\nu^{\ddagger}_{calcd}$, cm^{-1}	*kE* release,[a] kcal mol^{-1}
1 → **7**	16.8	13	4.9	4.5	1494	4.3
7 → HC≡CH	54.4	64	0	≤9.1	0	0
11 → **13**	47.0	55, 67	4.2	7.2, 20.1	457	~0
18 → **19**	83.3	80	55.3	53.1	2557	33
25 → **27**	81.0		52.5		1387	19
31 → **39**	45.8		12.5		1285	20

[a] References 8 and 9. [b] Reverse activation energy, kcal/mol.

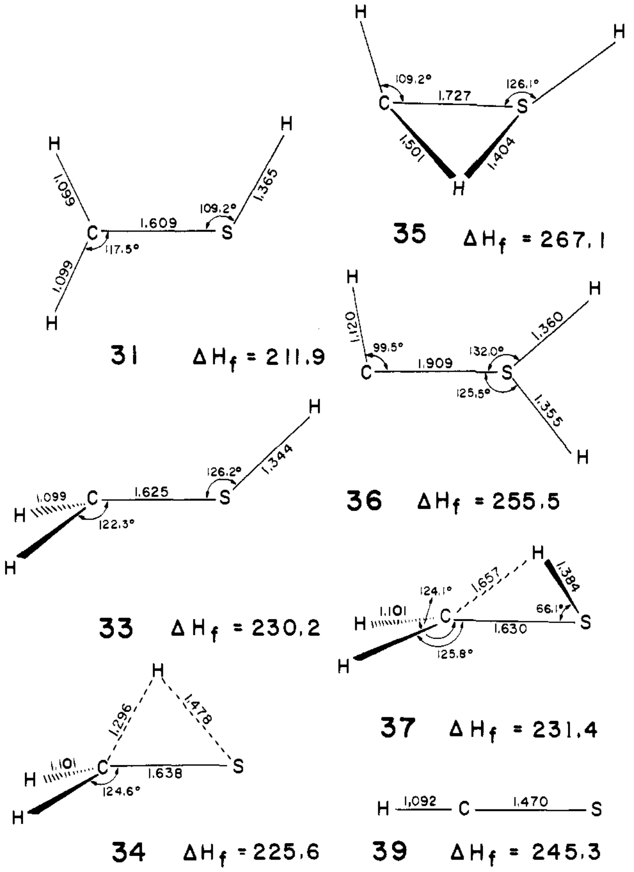


Figure 9. Calculated heats of formation and geometries for the CH_3S^+/CHS^+ system.

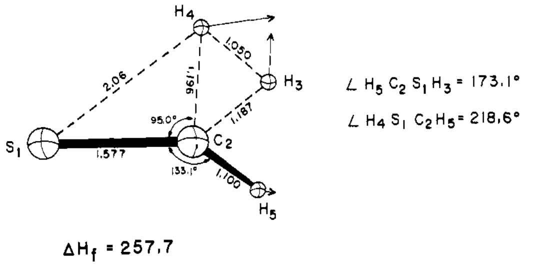


Figure 10. ORTEP plot of the transition state **38** for the elimination of molecular hydrogen from protonated thioformaldehyde.

thioformaldehyde is in accord with this observation. Here we can predict that no scrambling should occur, in agreement with experiment.[8]

Conclusions

The various thermochemical data for the reactions studied are summarized in Table III. Included are the vibrational frequencies corresponding to the negative eigenvalue of the force constant matrix for the transition states, and also the kinetic energy release observed in the products by Hvistendahl and Williams.[8,9] The interesting differences observed in the latter prompted us to investigate the details of our calculated potential surfaces further.

One possible explanation seemed to lie in variations in the internal vibrational energies of the reactants and products. MINDO/3 is of course parametrized to include an average allowance for these contributions to the total energy of a molecule, but fluctuations must arise and may indeed be partly responsible for the limited accuracy of MINDO/3. To check this possibility, we calculated the vibrational energies of the reactants and products in the usual way,[15] assuming a Boltzmann distribution of the energy levels. The relative vibrational energy contributions for reactant, transition state, and products were 1.7, 0, and −3.7 kcal/mol for the reaction **1** → (**7** + H_2); 4.8, 0, and −2.4 kcal/mol for the reaction **18** → (**19** + H_2); and 7.6, 0, and −1.6 kcal/mol for **11** → (**13** + H_2). These differences in the contributions are fairly small and are little correlated with the observed energy distribution in the products.

Of more significance is the apparent connection between the calculated frequencies of the imaginary modes for the transition states and the energy distributions reported for these reactions[8,9] (Table III). It appears from these results that the greater the curvature of the potential surface in the region of the transition state, the greater is the partitioning of the excess energy of the reaction into translational rather than vibronic modes. More quantitative estimates of the energy partitioning could be obtained from classical trajectory calculations using the MINDO/3 potential surface.[32]

MINDO/3 seems to have proven itself reliable in predicting the equilibrium geometries and fragmentation reactions of some simple organic cations, and the extension to larger mass spectral reactions of this type is certainly possible.

Acknowledgments. This work was supported by the Air Force Office of Scientific Research (Grant AFOSR 75-2749) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center. One of us (H.S.R.) thanks the Science Research Council (U.K.) for the award of a fellowship.

Supplementary Material Available: Cartesian coordinates for the structures mentioned in the text (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. Cone, M. J. S. Dewar, and D. Landman, *J. Am. Chem. Soc.*, **99**, 372 (1977).
(2) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, **99**, 2446 (1977).
(3) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, in press.
(4) (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975); (b) *ibid.*, **97**, 1294 (1975); (c) *ibid.*, **97**, 1302 (1975); (c) *ibid.*, **97**, 1307 (1975); (d) M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).
(5) M. J. S. Dewar and P. K. Bischoff, *J. Am. Chem. Soc.*, **97**, 2278 (1975).
(6) M. J. S. Dewar, R. C. Haddon, A. Komornicki, and H. S. Rzepa, *J. Am. Chem.*

Soc., **99**, 377 (1977).
(7) (a)See J. A. Pople, *Int. J. Mass Spectrom. Ion Phys.*, **17**, 1 (1976); (b) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11** (1974).
(8) (a) G. Hvistendahl and D. H. Williams, *J. Am. Chem. Soc.*, **96**, 6753 (1974); (b) *ibid.*, **96**, 6755 (1974); (c) *J. Chem. Soc., Chem. Commun.*, 4 (1975).
(9) G. Hvistendahl and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 881 (1975).
(10) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).
(11) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
(12) Using programs written by P. K. Weiner and A. Komornicki.
(13) S. Olivella, to be published.
(14) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).
(15) G. P. Ford, to be published.
(16) W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
(17) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).
(18) (a) For results and a discussion of theoretical calculations on ethane, see J. W. Rabalais and A. Katrib, *Mol. Phys.*, **27**, 923 (1974). (b) For a discussion on methane, see R. N. Dixon, *Mol. Phys.*, **20**, 113 (1971); R, Manne, *ibid.*, **24**, 935 (1972).
(19) J. Weber and A. D. McLean, *J. Am. Chem. Soc.*, **98**, 875 (1976).
(20) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
(21) M. L. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley-Interscience, New York, N.Y., 1968.
(22) J. W. McIver, *Acc. Chem. Res.*, **7**, 72 (1974).
(23) J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6682 (1975).
(24) M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).
(25) S. Saebø, *Chem. Phys. Lett.*, **40**, 462 (1976).
(26) Using a program written by C. E. Doubleday.
(27) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass. Spectrom. Ion Phys.*, 1, 1 (1968).
(28) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977).
(29) See footnote *b* in Table I.
(30) We used the GAUSSIAN 70 program as modified by A. Komornicki and W. Thiel.
(31) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, **53**, 1144 (1975).
(32) J. C. Polanyi and J. L. Schreiber, "Physical Chemistry", Vol. 6A, "The Kinetics of Gas Reactions", Chapter 6, Academic Press, New York, N.Y., 1974.

Gaseous Ions. 5.[1] Calculated (MINDO/3) Properties of Monosubstituted Tropylium Ions and Benzyl Cations

Michael J. S. Dewar* and David Landman[2]

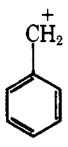
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.

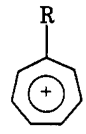
Received December 9, 1976

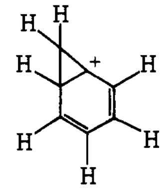
Abstract: Heats of formation, molecular geometries, and distributions of formal charge have been calculated by MINDO/3 for monosubstituted tropylium ions, and for monosubstituted benzyl cations with substituents in all possible positions (α, ortho, meta, para), for nine substituents (F, Cl, OH, NO_2, NH_2, CN, CH_3, ONO, OCH_3).

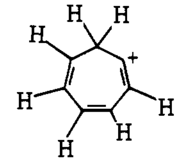
We recently reported[3] a MINDO/3[4] study of the conversion of benzyl cation (**1**) to tropylium (**2a**), a reaction which is believed to take place in the mass spectrometer. We concluded that it proceeds via two stable intermediates, the norcaradienium ion **3** and the cycloheptatrienium ion **4**. The calculated overall activation energy was quite high (32.7 kcal/mol), accounting for the failure to observe such rearrangements of benzyl cations in solution. We also studied the rearrangements of three derivatives (**5c–e**) of **1** to the corresponding tropylium ions (**2c–e**). The calculated properties of these ions were of interest from the point of view of the theory of substituent effects, the *p*-nitrobenzyl cation (**5e**) in particular having a nonplanar structure.

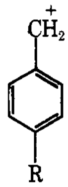
Recent experimental work[5] has suggested that derivatives of **1** may survive as such in the mass spectrometer under conditions where **1** itself is converted to **2**. The ions were obtained by loss of X from substituted toluene molecular ions of the type $(RC_6H_4CH_2X)^{+\cdot}$. Measurements of appearance potentials and wide range energy kinetics seemed to imply that when X = H, the resulting ions are benzylic if R = CH_3O, CH_3S, C_2H_5O, Cl, or Br, and tropenoid if R = CH_3, F, or OH; that when X = OPh the resulting ions are benzylic if R = CH_3O or NO_2 and tropenoid if R = CH_3, F, Cl, Br, or CF_3; and that when X = CH_3, the resulting ions are benzylic if R = NH_2 or CH_3O and tropenoid if R = OH, CH_3, F, Cl, Br, or CF_3. In the last case, however, comparisons of activation energies for loss of the methyl group from the precursor $(RC_6H_4C_2H_5)^{+\cdot}$ suggested that benzylic ions are also formed if R = F or CN and Lightner et al.[6] have claimed that benzylic ions are formed by loss of *n*-propyl from substituted *n*-butylbenzene molecular ions (i.e., X = *n*-Pr) if R = NH_2, CH_3O, HO, F, CH_3, CN, or NO_2.

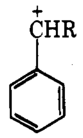

1

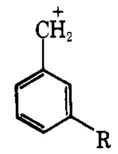

2a–k

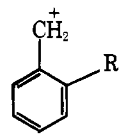

3


4


5b–k

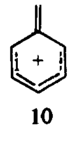

6b–k


7b–k

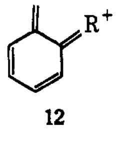

8b–k

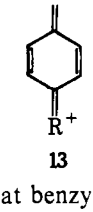
a, R = H; **b**, R = F; **c**, R = Cl; **d**, R = OH; **e**, R = NO_2; **f**, R = NH_2; **g**, R = CN; **h**, R = CH_3; **i**, R = ONO; **k**, R = OCH_3

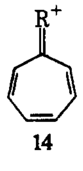

9


10


11


12


13


14

While these results seem to suggest that benzyl cation is stabilized relative to tropylium by $-E$[7] substituents such as NH_2 or OCH_3, there are several contradictory observations, for example, the claim that phenyl *p*-nitrobenzyl ether gave