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(3) Stereochemestry was assumed on the basis of the structure of the Diels–Alder adduct of 1 (ref 2).

(4) From $PhCF_3$ as internal standard; positive δ values are upfield.

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Threshold Photoionization and Dissociation of Toluene and Cycloheptatriene

Sir:

There has been some conjecture as to the threshold structure of the $C_7H_7^+$ ion formed by ionizing toluene and cycloheptatriene. From investigations using collisional activation mass spectra, McLafferty and Winkler[1] concluded that approximately equal abundances of benzyl and tropylium cations are formed from threshold energy decomposition, following a rapid equilibration between $C_7H_8^+$ ions with toluene and cycloheptatriene structures. Dunbar[2] also proposed that such a dynamic equilibrium was consistent with his photodissociation results for the toluene parent ion. However, the fraction of benzyl ion was observed to decrease to zero near the photodissociation threshold. This he interpreted in terms of the activation energy for dissociation being lower for the cycloheptatriene form of $C_7H_8^+$ than the toluene form. More recently, a MINDO calculation[3] has proposed that the easiest route for H loss from $C_7H_8^+$ for both toluene and cycloheptatriene is via the cycloheptatriene molecular ion to tropylium.

Appearance potentials can be used in conjunction with other thermochemical data as a means of determining possible structures of ions at threshold. However, in the case of $C_7H_7^+$ formed from toluene and cycloheptatriene there is a large kinetic shift associated with the decompositions which has resulted in previous overestimates of the appearance energies. This energy in excess of threshold, necessary for the ion to react sufficiently fast to be detected, can be minimized by increasing the ion source residence time[4] and/or increasing the detection sensitivity of the instrument. We wish to report here the use of a photoionization mass spectrometer and associated signal-averaging techniques which has enabled the measurement of $AP(C_7H_7^+)$ from toluene and cycloheptatriene at high sensitivity.

The instrument used in the present experiments consists of a windowless hydrogen discharge lamp and 1-m Seya–Namioka monochromator[5] attached to a 15-cm single-focusing mass spectrometer. A microprocessor is used for the on-line control and extended signal averaging of experimental data needed to achieve a high sensitivity of detection. A detailed description of the photoionization mass spectrometer will form part of a later publication.[6]

The photoionization efficiency curve for $C_7H_7^+$ produced from toluene is shown in Figure 1. Using the method of interpretation of photoionization data described by Guyon and Berkowitz,[7] we obtain an appearance energy of 10.71 ± 0.03 eV. This is in excellent agreement with the results of Gordon and Reid[4] who obtained a limiting value of 10.70 eV at ion source residence times in excess of 900 μs. The corresponding appearance energy for cycloheptatriene (Figure 2) is found to be 9.36 ± 0.02 eV. Combining the heats of formation for the neutral species[8] in the reaction $C_7H_8 + h\nu \rightarrow C_7H_7^+ + H + e +$ (excess energy) with the observed appearance energies, and neglecting any excess energy contribution, gives heats of formation for $C_7H_7^+$ of 206.9 ± 0.7 kcal/mol and 207.6 ± 0.5 kcal/mol from toluene and cycloheptatriene, respectively. The kinetic energy release accompanying both processes has been measured from metastable studies[9] to be 4.0 kcal/mol which probably represents an upper limit to the reverse activation energy. A recent MINDO calculation[3] indicates that the reverse activation energy is indeed small, giving an estimate of only 1.4 kcal/mol.

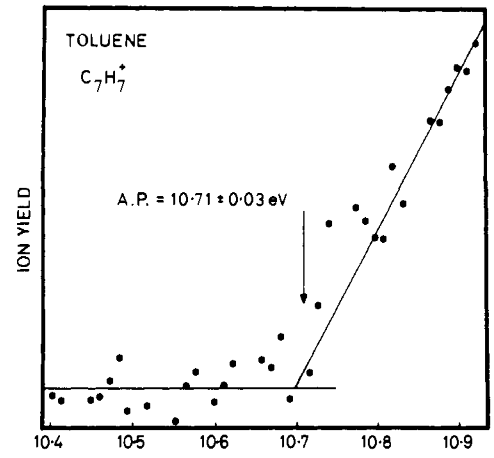

Figure 1. Threshold photoionization efficiency curve for formation of $C_7H_7^+$ ion from toluene.

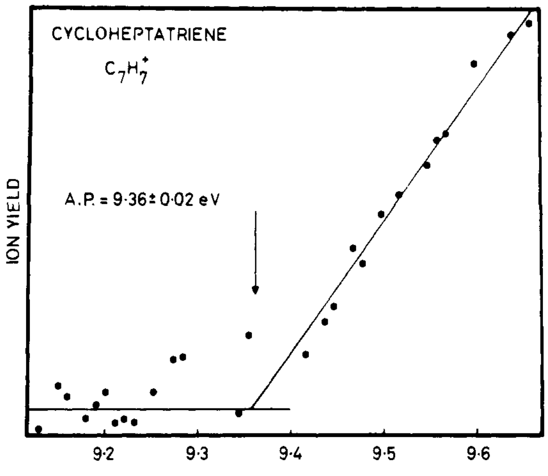

Figure 2. Threshold photoionization efficiency curve for formation of $C_7H_7^+$ from cycloheptatriene.

Lossing[10] has measured the adiabatic ionization energy for the benzyl radical by electron impact to be ≤7.27 eV which is in good agreement with a recent corresponding photoelectron spectroscopic value of 7.20 ± 0.03 eV.[11] If ΔH_f(benzyl) is taken as 45 kcal/mol,[12] one obtains $\Delta H_f(\text{benzyl}^+) = 211$ kcal/mol which is lower than either a recent ab initio calculation of 217.1 kcal/mol[13] or a MINDO calculation of 220.4 kcal/mol.[14] It is also lower than the value of 219 ± 4 kcal/mol obtained by Jackson, Lias, and Ausloos[15] who used ion cyclotron resonance spectroscopy to measure the rate constants for reaction of benzyl ion with a number of alkanes and cycloalkanes. It thus appears that from an energetic viewpoint the $C_7H_7^+$ ion formed at threshold for toluene and cycloheptatriene cannot have the benzyl structure.

Our value of 207 kcal/mol is in good agreement with the theoretical calculation for tropylium ion by Abboud, Hehr, and Taft[13] (207.9 kcal/mol) and ionization energy measurements of the tropyl radical[16,17] (209 kcal/mol), but is at variance with the MINDO value of 195.6 kcal/mol.[14] Dewar and coworkers[14] have suggested that the heat of formation derived from the tropyl radical ionization potential could be due to a large difference between the vertical and adiabatic values. However, neither Thrush and Zwolenik[16] nor Elder and Parr[17] observed vibrational structure in their data to support this proposal. A much larger uncertainty than the ionization potential is the heat of formation of the tropyl radical with estimates ranging from 64.8 kcal/mol[18] to 71.3 kcal/mol.[19]

In conclusion, we feel that our results confirm that the $C_7H_7^+$ ion formed at threshold for both toluene and cycloheptatriene has the tropylium structure. We also propose that the heat of formation for tropylium cation is not significantly lower than our observed value of 207 kcal/mol.

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Role of the Dispersion Energy in the Binding of the $(Cl_2)_2$ Molecule

Sir:

While the Cl_2 crystal has been the subject of many experimental and theoretical studies, the interest in the $(Cl_2)_2$ dimer is much more recent. In 1974, Klemperer et al.[1] observed that the $(Cl_2)_2$ dimer is polar, such a polarity being compatible with an "L-shaped" or a "T-shaped" structure. Two theoretical studies,[2,3] based on the use of molecular orbitals, attempted to determine the most stable configuration. Unfortunately, in both cases, either the method used or practical limitations involved in the treatment led to unconclusive results. In the first case,[2] the method used was not appropriate for the treatment of such weakly bonded molecules since the electron correlation effect is neglected. As we shall show, the dispersion energy contribution is predominant in the binding of the $(Cl_2)_2$ dimer. Thus the binding energies obtained[2] are artificial. In ref 3, the $(F_2)_2$ dimer is considered as a model, assuming a similar structure for $(F_2)_2$ and $(Cl_2)_2$. Using ab initio wave functions, the dispersion energy is added to the SCF supermolecule treatment. These calculations give a linear configuration more stable than the T-shaped one. This does not agree with the experimental observation.[1,3] As we shall show this disagreement is probably due to a bad description of the dispersion energy in ref 3, this description being better in the case of the linear configuration than in the T-shaped one.

Table I. $(Cl_2)_2$: Intermolecular Energies (kcal/mol)

Configuration	d, Å[a]	ΔE_{SCF}[b]	E_{disp}[c]	E'_{disp}[d]	E_{tot}[e]
Linear	3.175	2.10	−2.49	−1.86	−0.39
	3.440	1.10	−1.61	−1.20	−0.51
	3.969	0.45	−0.73	−0.54	−0.29
	4.763	0.19			
"T-Shaped"	3.175	1.69	−3.25	−2.44	−1.56
	3.440	0.43	−2.11	−1.58	−1.68
	3.704	−0.01	−1.40	−1.05	−1.41
	4.233	−0.11			
	4.763[f]	−0.00			

[a] See ref 3, Figure 5: in the linear case, d is the distance between the two nearest nonbounded atoms; in the "T-shaped" one, d is the distance between the middle of molecule 1 (see in the text) and the nearest atom of molecule 2. [b] $\Delta E_{SCF} = E_{SCF}(\text{dimer}) - E_{SCF}(\text{isolated molecule})$. [c] Expression 2 of ref 5. [d] Expression 1 of ref 5 and used in ref 3. [e] $E_{tot} = \Delta E_{SCF} + E_{disp}$. [f] Using a double ζ basis set.

Though our own calculations on the $(Cl_2)_2$ dimer are not yet completed, our preliminary results show the importance of the dispersion energy and explain the difficulties encountered in ref 3. In the present communication, we give the results obtained for two configurations: the linear one and the T-shaped one. As in our previous studies of the $(H_2)_2$ system,[4] a perturbation dispersion term[5] is added to the SCF supermolecule energies.[6] Two expressions of the dispersion term have been proposed,[5] corresponding to different partitions of the individual molecular hamiltonians: expression 2 is used in the present work, denoted E_{disp} in Table I; expression 1 is used in ref 3, denoted E'_{disp} in Table I.

Ab initio calculations are then performed, using molecular orbitals which are linear combinations of gaussian functions centered on each atom. For the SCF supermolecule treatment a large basis set is used: 11s and 7p uncontracted functions taken from ref 7 and a d function chosen to optimize the energy of the Cl_2 molecule. The energy of the Cl_2 molecule is 918.9077 hartrees for an optimized distance of 2.011 Å. This distance can be compared with the experimental value of 1.988 Å. For the calculation of the dispersion energy, the previous basis set is contracted into one function for each shell of the core (1s, 2s, 2p) and two functions for the valence shells (3s, 3p). The d polarization function is now optimized in order to obtain the largest value of the dispersion energy, as previously described for other systems.[4,5] In the calculation of the dispersion energy, the core shells are not taken into account. The molecular distances are not varied in the calculations.

For the linear configuration ΔE_{SCF} (Table I) is repulsive at intermediate intermolecular distances ($d \lesssim 4.763$ Å) and very probably replusive at larger distances. For the T-shaped configuration ΔE_{SCF} becomes attractive around $d = 3.7$ Å, the attractive energy being −0.113 kcal/mol for $d = 4.233$ Å. We have not tried to determine the SCF minimum with more accuracy since the van der Waals minimum is located at shorter distances. Our results are in disagreement with the study of the $(F_2)_2$ system which exhibits an SCF minimum for the two configurations.[3] However, a smaller basis set gives less repulsive energies for both configurations of $(Cl_2)_2$. Also the intermolecular SCF energy is very sensitive to the optimization of the molecular distance. Thus we may wonder whether both dimers have a different behavior or if a larger basis set would give an attractive SCF intermolecular energy for the linear configuration of the $(F_2)_2$ system.

We can see from Table I that the values of E'_{disp} are about 75% of those of E_{disp}. An analysis of the contribution due to the different molecular orbitals shows the importance of d orbitals. Let us consider the T-shaped configuration: the first