ab initio method. By application of the Hammond postulate it is possible to properly weigh reactant and product properties when describing the TS.

As long as direct calculations of TS's of complex reactions are not feasible at the required level of accuracy, ab initio calculations of reaction intermediates, formed or decomposed in the TS under consideration, can provide an important insight into the reaction mechanisms.

In the case of ozonolysis special consideration has to be given to the conformational processes of the molecules involved. Thus it is not sufficient to calculate just the most stable PO forms. For the fluorinated PO's **4**–**6** the barriers for conformational changes are predicted to be lower than those for decomposition. According to the Curtin–Hammett principle[28] the higher molecular populations at $\phi = 0°$ are immaterial when looking for the conformers that lead to either syn or anti CO. Instead, those PO forms have to be investigated which are expected to be closest to the TS. In this connection, the assumption of concertedness of reactions I–III is reasonable and helpful.[8] Observing these principles, the stereochemical features of the ozonolyses of **1**–**3** can be traced to the following electronic effects.

(1) The $\pi$ donor and $\sigma$ acceptor ability of F leads to stabilization of PO, CO, aldehyde, and FO. Stabilization is highest for the aldehyde due to the marked $\pi$ acceptor property of the C=O group.

(2) $\pi$ donation from an equatorial F destablizes puckered PO's and FO's. This statement is rephrased by saying that fluorine prefers the axial site in ozonides due to favorable anomeric interactions.

(3) Repulsion between the negatively charged F and the terminal O weakens the syn effect observed for CO's.[21]

Because of (1) decomposition of **4**–**6** is an exothermic step with an early TS. Because of (2) PO's should preferentially cleave via conformers leading to syn CO. Dipole–dipole attraction in TS III favors the formation of trans difluoro FO. Since this applies to both syn and anti CO, the cis–trans FO ratio is unusually low. This was first noted by Gilles.[4] Qualitative arguments put forward on the basis of the orbital symmetry analysis[4,6] are essentially verified by our ab initio results.

**Acknowledgment.** I thank Professor R. L. Kuczkowski for suggesting this work. Special acknowledgment is made to the Rechenzentrum Köln for providing computation time on CDC CYBER 76.

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# Negative Ion States of Terminal Methyl-Substituted Butadienes. Evidence for Through-Space Interactions Involving Methyl Groups

**Stuart W. Staley,*[1a] Judith C. Giordan,[1b] and John H. Moore*[1b]**

*Contribution from the Departments of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588, and University of Maryland, College Park, Maryland 20742.*

*Received August 11, 1980*

**Abstract:** Gas-phase attachment energies, corresponding to the energies of the first and second antibonding $\pi$ orbitals of terminal methyl-substituted butadienes, were determined by electron-transmission spectroscopy. The data provide evidence for a significant through-space interaction between the hydrogen orbitals of the methyl group and the diene $\pi$ system and suggest conclusions regarding the conformations of the methyl groups.

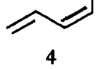
The effect of methyl hyperconjugation on the thermodynamic, kinetic, and spectroscopic properties of $\pi$ electron systems has been of continuing interest for over 4 decades. The purpose of this study is to evaluate the effect of terminal methyl substitution on the energies of the lowest two ($\pi^*$) negative ion states of 1,3-butadiene. As will be seen, the relatively diffuse character of negative ion states permits the observation of long-range or "through-space" electronic effects which are often not observed in neutral molecules or cations.

The energies of the negative ion states associated with the unfilled $\pi^*$ orbitals of 1,3-butadiene (**1**), *trans*-1,3-pentadiene (**2**), *trans,trans*-2,4-hexadiene (**3**), *cis*-1,3-pentadiene (**4**), and *cis,cis*-2,4-hexadiene (**5**) have been measured by electron-transmission spectroscopy. This technique[2,3] allows for the capture of low-energy (0–10 eV) electrons by a target molecule in the gas phase for periods on the order of $10^{-14}$ s. The formation of a transient negative ion is observed as a sharp structure or "resonance" in the total electron-scattering cross section as a function of energy.


1


2


3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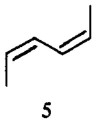
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Table I. Electron Affinities and Attachment Energies of Butadiene and Terminal Methyl-Substituted Butadienes

| compound | $EA_1$[a] | $AE_1$[b] | $AE_2$[c] |
|---|---|---|---|
| 1,3-butadiene (1) | −0.65 | 0.76 | 2.8 |
| | −0.62[d] | 0.62[d] | 2.8[d] |
| *trans*-1,3-pentadiene (2) | | 0.95 | 2.8 |
| *trans,trans*-2,4-hexadiene (3) | | 1.13 | 2.8 |
| *cis*-1,3-pentadiene (4) | | 0.86 | 3.1 |
| *cis,cis*-2,4-hexadiene (5) | | 0.96 | 3.2 |

[a] First electron affinity (±0.05 eV). [b] First attachment energy (±0.05 eV). [c] Second attachment energy (±0.1 eV). [d] Reference 4.

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[1] (a) University of Nebraska–Lincoln; (b) University of Maryland.

[2] (a) L. Sanche and G. J. Schulz, *Phys. Rev. A*, **5**, 1672 (1972); (b) K. D. Jordan and P. D. Burrow, *Acc. Chem. Res.*, **11**, 341 (1978).

[3] J. C. Giordan, M. R. McMillan, J. H. Moore, and S. W. Staley, *J. Am. Chem. Soc.*, **102**, 4870 (1980).

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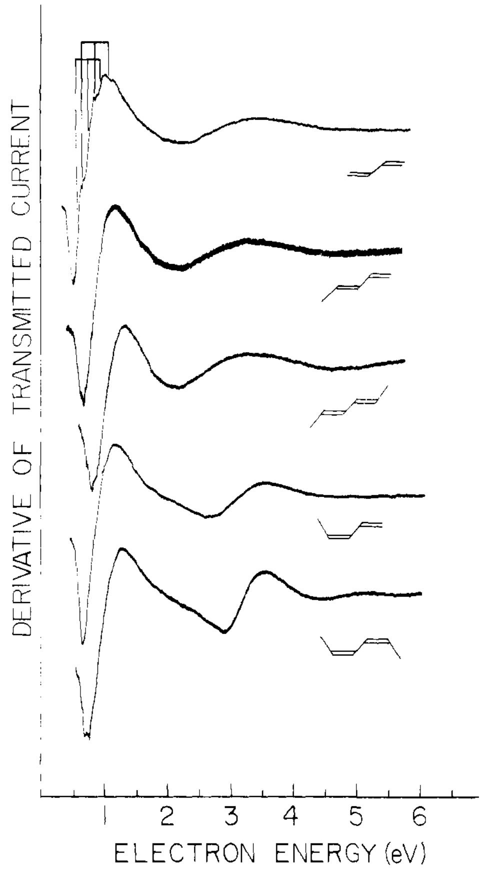


**Figure 1.** Spectra of **1–5** presented as the derivative of the transmitted electron current vs. electron energy. The 1.98 eV feature in the spectrum of nitrogen was used to calibrate these spectra.

Resonances are manifested as sharp variations in the transparency of the gas to an electron beam. The electron impact energies at which resonances occur correspond to the attachment energies (AEs) of the molecule.[3] If the lifetime of the anion is sufficiently long, "vibrational" bands may be apparent within the resonance, and the adiabatic electron affinity (EA) may then be equated to the negative of the energy of the first vibrational band.

## Results

Figure 1 shows the electron-transmission spectra of compounds **1–5** obtained with an instrumental resolution of ca. 50 meV. In order to accentuate small variations in these spectra, the first derivative of the transmitted current as a function of energy is presented. It can be seen that only the negative ion formed from electron capture of 1,3-butadiene (**1**) is sufficiently long lived to possess vibrational structure.[4] The two resonances observed in each of the spectra of compounds **1** through **5** arise from the capture of the incident electron into the unoccupied $\pi$ orbitals, $\psi_3^*$ and $\psi_4^*$. As expected, the resonances corresponding to $\psi_4^*$ are broader than those for $\psi_3^*$. This is in part due to the greater energy of an electron in the former orbital which results in a shorter lifetime of the corresponding negative ion state.[2]

The data from Figure 1 are summarized in Table I. If one assumes the validity of Koopmans' theorem,[6] then the relative AEs can be equated to the relative SCF orbital energies. The correlation diagram in Figure 2 displays the negative of the attachment energies and the ionization potentials. This figure suggests that $\psi_3^*$ and $\psi_4^*$ can be destabilized, stabilized, or unchanged in energy on addition of methyl groups, depending on the circumstances. Systematic evaluation of these changes demonstrates some novel through-space orbital interactions.

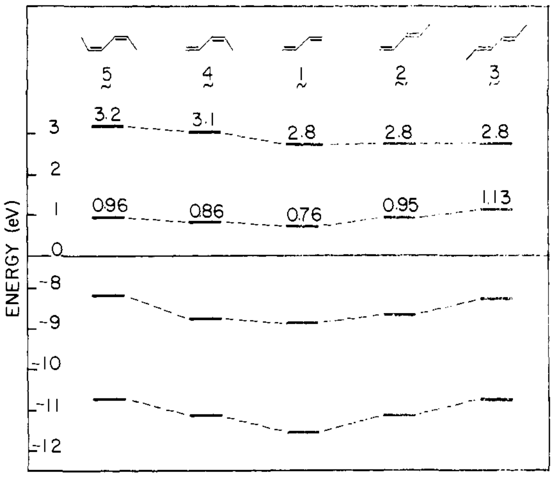


**Figure 2.** Correlation diagram for the $\pi$ and $\pi^*$ orbitals of **1–5**. The energies of the bonding orbitals are based upon photoelectron spectroscopic data (ref 5).

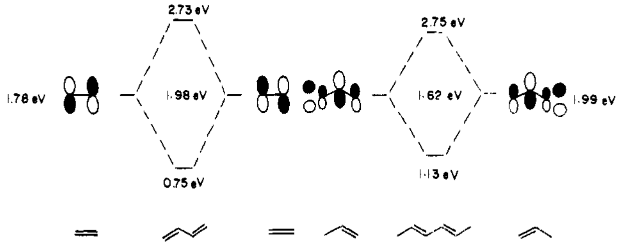


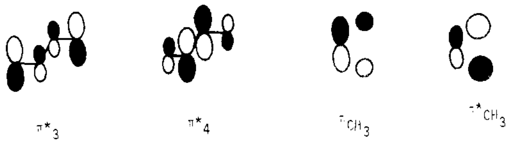
**Figure 3.** Diagram showing the interaction of $\pi^*$ of ethene (**6**) and propene (**7**) to form $\psi_3^*$ and $\psi_4^*$ in **1** and **3**, respectively. Interactions with other orbitals in **6** and **7** are ignored.

## Discussion

According to perturbation theory, the change in energy ($\Delta\epsilon$) of an orbital $\psi_a$ due to interaction with a second orbital $\psi_b$ is given by

$$\Delta\epsilon = \frac{\langle\psi_a|\mathcal{H}'|\psi_b\rangle^2}{\epsilon_a - \epsilon_b} \tag{1}$$

where $\psi_a$ and $\psi_b$ are the unperturbed basis orbitals of energy $\epsilon_a$ and $\epsilon_b$, respectively, and H′ is the interaction Hamiltonian. In other words, two orbitals will interact strongly if they overlap to a large extent and are of similar energy. In this study, the basis orbitals are $\pi_3^*$ and $\pi_4^*$ of the diene unit and the methyl group orbitals of $\pi$ symmetry, $\pi_{CH_3}$ and $\pi_{CH_3}^*$.



***trans*-Methyl Substitution.** We have chosen two approaches in order to evaluate the effect of terminal methyl substitution on butadiene. One approach entails the mixing of two ethene (**6**) or two propene (**7**) $\pi^*$ orbitals to form $\psi_3^*$ and $\psi_4^*$ of butadiene (**1**) or *trans,trans*-2,4-hexadiene (**3**), respectively. As seen in Figure 3, the split between attachment energies associated with $\psi_3^*$ and $\psi_4^*$ ($\Delta\psi^*$) in **3** is ca. 0.36 eV less than $\Delta\psi^*$ in **1**. This can be understood as follows. The lowest $\pi^*$ orbital in propene ($AE_1$ = 1.99 eV)[2b] is constructed by mixing $\pi^*$ of **6** ($AE_1$ = 1.79 eV)[2b] with $\pi_{CH_3}$ and $\pi_{CH_3}^*$ and, through these oritals, with $\pi$ of **6**. This mixing produces a polarization of the double bond such that $c_2 > c_1$ in $\pi$ and $c_1 > c_2$ in $\pi^*$, where $c_1$ and $c_2$ are the coefficients of the orbitals at $C_1$ and $C_2$, respectively.[7] In view of the relative magnitudes of $c_1$ in **6** and **7** (see Figure 3), it is

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[4] P. D. Burrow and K. D. Jordan, *Chem. Phys. Lett.*, **36**, 594 (1975).

[5] G. Bieri, F. Burger, E. Heilbronner, and J. P. Maier, *Helv. Chim. Acta*, **60**, 2213 (1977).

[6] T. Koopmans, *Physica*, **1**, 104 (1934).

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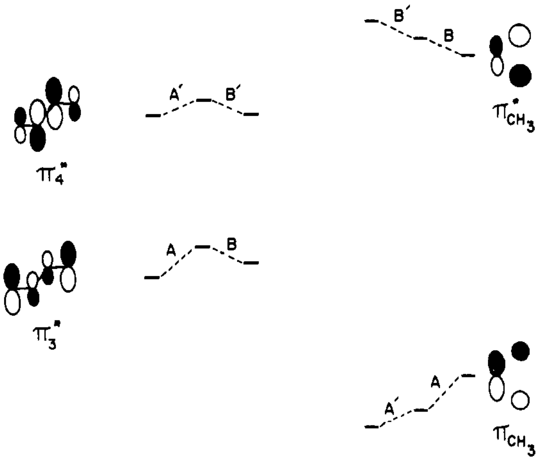


**Figure 4.** Diagram showing interaction of $\pi_3^*$ and $\pi_4^*$ of a diene unit with the pseudo-$\pi$ orbitals of a methyl group ($\pi_{CH_3}$ and $\pi_{CH_3}^*$). A and A′ are antibonding interactions whereas B and B′ are bonding interactions.

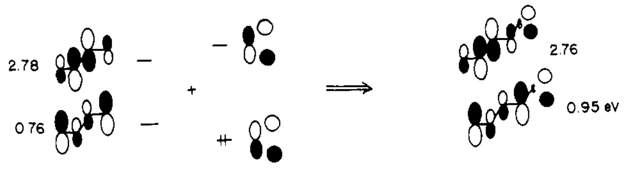


**Figure 5.** Antibonding $\pi$ orbitals ($\psi_3^*$ and $\psi_4^*$) of 2 as derived by comparing values of $AE_1$ and $AE_2$ in 1 with the corresponding values in 2.

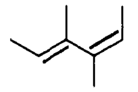
reasonable that $\Delta\psi^*$ is less in 3 than in 1.

A second approach shows the construction of $\psi_3^*$ and $\psi_4^*$ for *trans*-1,3-pentadiene (2) from the $\pi$ orbitals of butadiene and a methyl group, as illustrated in Figure 4. The final $\pi$ orbitals ($\psi_3^*$ and $\psi_4^*$) of 2 arise through antibonding interactions (A and A′, respectively) with $\pi_{CH_3}$ and bonding interactions (B and B′, respectively) with $\pi_{CH_3}^*$. Note that $\pi_3^*$, which is closer to $\pi_{CH_3}^*$ than is $\pi_4^*$, is more destabilized than $\pi_4^*$.

The above considerations lead to the conclusion that $\psi_3^*$ and $\psi_4^*$ of 2 can be represented as in Figure 5. This figure utilizes the favored "eclipsed" conformation of 2 (one methyl H is eclipsed with the $C_3$–$C_4$ double bond).[8] Several important points are illustrated in Figure 5. First, note that the hydrogen wave functions in $\pi_{CH_3}$ and $\pi_{CH_3}^*$ reinforce each other through interactions A and B or A′ and B′ whereas the methyl carbon wave functions tend to cancel. Since the phases of the methyl hydrogen wave functions in $\psi_4^*$ must be as indicated in Figure 5, the fact that $AE_2$ is unchanged on going from 1 to 2 or 3 requires that the *p*($\pi$) coefficient of the wave function at the methyl carbon be either (a) essentially zero if there is no significant antibonding interaction between the $C_4$ p($\pi$) orbital and the methyl hydrogen 1s orbitals in $\psi_4^*$ or (b) small, but in phase (bonding) with the $C_4$ p($\pi$) orbitals if the $C_4$ p($\pi$)–H 1s antibonding interaction is significant. The latter points are the key to understanding the data for 4 and 5.

***cis*-Methyl Substitution.** Terminal *cis*-methyl substitution, as in 4 and 5, would be expected to cause the same hyperconjugative interactions as discussed for 2 and 3 due to interaction with the terminal p orbital(s) of the diene system. However, as seen in Figure 2, cis substitution destabilizes $\psi_3^*$ less and $\psi_4^*$ more than does *trans*-methyl substitution. A related observation is that the splitting of the attachment energies associated with $\psi_3^*$ and $\psi_4^*$ in 5 is 0.2 eV *greater* than in 1, rather than 0.4 eV less, as in 3. Clearly an additional effect is present in 4 and 5 compared to 2 and 3.

We first consider possible structural factors associated with the diene unit. An increase or decrease in the double bond lengths or a twisting about the double bonds[9] in 5 relative to 3 can be dismissed since this would cause *both* $\psi_3^*$ and $\psi_4^*$ to be lowered or raised simultaneously. However, a decrease in the length of the $C_2$–$C_3$ single bond in 4 (or the $C_3$–$C_4$ single bond in 5) would cause a shift of $\psi_3^*$ and $\psi_4^*$ in the observed directions. The detailed structures of these compounds are not known but it has been reported that $C_3$–$C_4$ in 8 is, if anything, *longer* than $C_3$–$C_4$ in 9,[10] although the difference is well within the experimental uncertainty. In any case, there appears to be no compelling reason for $C_2$–$C_3$ to be shorter in 5 than in 3.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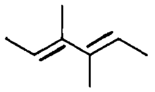
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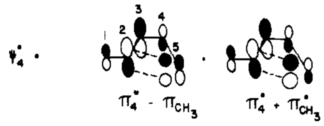
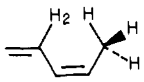


**Figure 6.** Construction of $\psi_4^*$ of 4b through $C_4$ p($\pi$)–$C_5$ p($\pi$) and $C_2$ p($\pi$)–H 1s ($\pi$) interactions between $\pi_4^*$ and $\pi_{CH_3}$ or $\pi_{CH_3}^*$.

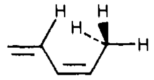
A twisting of the diene unit around the $C_2$–$C_3$ bond from a coplanar arrangement in 4 or 5 to a noncoplanar conformation in 2 or 3 would have a similar effect. However, current evidence indicates that 2 possesses a coplanar diene unit.[8,11,12] Furthermore, simple steric considerations suggest that 4 and 5 are more likely to have a twisted diene unit than are 2 and 3, and this would produce a decrease in the splitting between $AE_2$ and $AE_1$[3] rather than an increase, as observed.

In summary, we conclude that none of the above structural changes provides an adequate basis for understanding the data in Figure 2 and that we must look elsewhere for a rationale for the relative values of $\psi_3^*$ and $\psi_4^*$ in these isomers.

Our view is that through-space interactions are operative in 4 and 5. Such interactions can be evaluated as follows. Consider first $\psi_4^*$ in 2 (Figure 5). If the methyl group is moved from the trans to the cis position and kept in the conformation in which the methyl hydrogen is eclipsed with the double bond (4a),[8] then the following interactions of $\pi_{CH_3}$ and $\pi_{CH_3}^*$ with $\pi_4^*$ of the diene unit occur. (a) No changes take place in the interaction between the $C_3$ and $C_4$ p($\pi$) orbitals and the methyl C p($\pi$) orbital if $\angle CH_3$–$C_4$–$C_3$ remains the same. (b) The interaction between the $C_2$ p($\pi$) orbital and the methyl C p($\pi$) orbital is either zero or slightly stabilizing. (c) The $C_1$ p($\pi$)–methyl C p($\pi$) interaction is negligible due to the distance involved.



4a



4b

Clearly the methyl C p($\pi$) orbital cannot play a role in the observed destabilization of $\psi_4^*$. This destabilization must therefore result from an additional interaction of the diene $\pi$ system with hydrogen orbitals of $\pi_{CH_3}$ and $\pi_{CH_3}^*$ on going from 2 to 4. However, such an interaction would be small or negligible in conformation 4a due to the distance of the out-of-plane hydrogen atoms from the $\pi$ sytem. We therefore draw the additional conclusion that *at least one of the out-of-plane methyl hydrogens*

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[8] This is calculated to be the lowest energy conformation by force-field calculations: H. Dodziuk, *J. Mol. Struct.*, **10**, 275 (1971).

[9] R. Grinter and T. L. Threlfall, *Tetrahedron*, **35**, 1543 (1979).

[10] M. Traetteberg, *Acta Chem. Scand.*, **24**, 2295 (1970).

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[12] D. A. C. Compton, W. O. George, and W. F. Maddams, *J. Chem. Soc., Perkin Trans. 2*, 1311 (1977).

[13] Note that Figure 6 is constructed under the assumption that the $C_4$ p($\pi$)–$C_5$ p($\pi$) interaction in $\pi_4^* + \pi_{CH_3}^*$ is greater than the opposing H 1s ($\pi$)–$C_2$ p($\pi$) interaction. In the unlikely event that the opposite is true, then $\pi_4^* - \pi_{CH_3}^*$ would represent the appropriate stabilizing interaction. In either case the opposite effects of these two interactions will result in a destabilization of $\pi_4^*$ in 4 which is not present in $\pi_4^*$ of 2.

*must be directed toward $C_2$ of the diene system* (i.e., must be an interior methyl H). This would result in a through-space interaction of the $C_3$ p($\pi$) orbital and, more importantly, the $C_2$ p($\pi$) orbital with a hydrogen 1s orbital (or orbitals) which would account for the observed destabilization of $\psi_4^*$. The major interaction is illustrated in Figure 6 for conformation **4b**, although there are clearly an infinite number of conformations with interior out-of-plane methyl hydrogens which would account for this observation. (The occurrence of such conformations can be rationalized on the basis of an interaction between the eclipsed methyl hydrogen and $H_2$ in conformation **4a.**) A similar through-space interaction accounts for the *relative* stabilization of $\psi_3^*$ in **4** and **5** compared to **2** and **3**, respectively. Indeed the agreement of the *relative* trans–cis shifts of *both* $\psi_3^*$ and $\psi_4^*$ with the foregoing through-space interaction is an important factor in support of this analysis.

The long-wavelength electronic-absorption band for the negative ions of **1**, **3**, and **4**, prepared by $\gamma$-irradiation in methyltetrahydrofuran glasses at −196 °C, has been attributed to a transition between $\psi_3^*$ and $\psi_4^*$.[14] The energies of these transitions (2.18, 2.16, and 2.20 eV, respectively) are in the same relative order as are the values of $AE_2 - AE_1$ (2.02, 1.65, and 2.21 eV, respectively), but the differences are greatly attenuated. This observation might be attributed to a substantial amount of diffuse character in these negative ion states which is greatly diminished in condensed phases.[15,16]

**Summary.** The key findings of the present investigation are (a) that significant through-space methyl-$\pi$ interactions exist in the $\psi_3^*$ and $\psi_4^*$ negative ion states of **4** and **5**, (b) the this interaction in $\psi_4^*$, and probably also in $\psi_3^*$, primarily involves the hydrogen 1s ($\pi$) rather than the carbon p($\pi$) orbital of the methyl group, and (c) that conformations with interior out-of-plane methyl hydrogens make a significant (but as yet unspecified) contribution to the distribution of conformations in **4**. Similar considerations also apply to **5**. We believe that the electron-transmission technique may prove to be quite powerful in probing certain conformational questions. This will serve to greatly expand its already recognized importance in providing electron affinities and attachment energies of complex molecules.

**Acknowledgment.** We thank the National Science Foundation (Grant No. CHE77-14930) for support of this work and the Gillette Research Foundation for a fellowship to J.C.G.

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[15] M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. 1, Academic Press, New York, 1974, pp 76–91.

[16] K. D. Jordan and P. D. Burrow, *Chem. Phys.*, **45**, 171 (1980).

# Thermoneutral Isotope Exchange Reactions of Cations in the Gas Phase

**P. Ausloos* and S. G. Lias**

*Contribution from the National Bureau of Standards, Washington, D. C. 20234.*
*Received August 25, 1980*

**Abstract:** Rate constants have been measured for reactions of the type $AD_2^+ + MH \rightarrow MD + ADH^+$, where $AD_2^+$ is $CD_3CND^+$, $CD_3CDOD^+$, $(CD_3COCD_3)D^+$, or $(C_2D_5)_2OD^+$ and the MH molecules are alcohols, acids, mercaptans, $H_2S$, $AsH_3$, $PH_3$, or aromatic molecules. Rate constants are also presented for the reactions $Ar_HD^+ + D_2O \rightarrow Ar_DD^+ + HDO$, where $Ar_HD^+$ is a deuteronated aromatic molecule and $Ar_DD^+$ is the same species with a D atom incorporated on the ring. In all but two cases, the competing deuteron transfer is sufficiently endothermic that it cannot be observed under the conditions of the ICR experiments at 320–420 K. The efficiencies of the isotope exchange reactions are interpreted in terms of estimated potential surface cross sections for the reactions $AD_2^+ + MH \rightarrow [AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+] \rightarrow [ADH^+{\cdot}MD] \rightarrow ADH^+ + MD$. When the formation of the $[AD{\cdot}MHD^+]$ complex is estimated to be thermoneutral or slightly endothermic, the isotope exchange process is inefficient (probability of a reactive collision < 0.1) or does not occur. The most efficient isotope exchange reactions are observed for those systems for which it is estimated that the transformation $[AD_2^+{\cdot}MH] \rightarrow [AD{\cdot}MHD^+]$ is exothermic. For most of the systems, trends in reaction efficiency appear to be related to factors such as dipole moments of reactant species (or for aromatic compounds, the electron-donating or -withdrawing properties of ring substituents) which influence the relative orientation of the two reactant species in the complex.

In 1975, Freiser, Woodin, and Beauchamp[1] reported the observation of isotope exchange reactions involving protonated (deuteronated) aromatic molecules and $D_2O$. The sequence:

$$C_6H_6D^+ + D_2O \rightarrow C_6H_5D_2^+ + HDO \qquad (1a)$$

$$C_6H_5D_2^+ + D_2O \rightarrow C_6H_4D_3^+ + HDO \qquad (1b)$$

and analogous sequences involving other aromatic species were seen to continue until all H atoms on the aromatic ring were replaced by D atoms. They proposed that ring protonation was a necessary condition for exchange, and suggested that the mechanism involved the occurrence of a proton transfer to $D_2O$ *in the complex*, followed by dissociation of the complex to form HDO, since formation of separated $HD_2O^+$ is endothermic for these reactions.

Martinsen and Buttrill[2] investigated such isotope exchange reactions involving protonated (deuteronated) aromatic species and $D_2O$ in a high-pressure mass spectrometer, and reported observations and conclusions essentially in agreement with those of the ion cyclotron resonance study.[1]

More recently, Hunt and collaborators[3] have examined such reactions in conjunction with work on chemical ionization mass

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[1] Freiser, B. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 6892.

[2] Martinsen, D. P.; Buttrill, S. E., Jr. *Org. Mass Spectrom.* **1976**, *11*, 762.

[3] (a) Hunt, D. F.; Sethi, S. K. *J. Am. Chem. Soc.* **1980**, *102*, 6953. (b) Hunt, D. F.; Sethi, S. K.; Shabanowitz, J., presented at the 26th Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, MO, May 28–June 2, 1978. (c) Hunt, D. F.; Sethi, S. K., presented at the 27th Annual Conference on Mass Spectrometry and Allied Topics, Seattle, WN, June 3–8, 1979.