only the non-fixed energy of the transition state is available in (2). The mechanistically based model suggested here to account for these results is certainly not the only one capable of doing so. It is, however, consistent with some of the limited available data on the dissociation dynamics of polyatomic molecules and the basic trends observed in the photochemistry and photophysics of polyatomics. We are presently studying energy disposal dynamics in the fragmentation reactions of several other cyclic ketones. The data thus obtained will be useful in evaluating further the mechanistic/dynamical model outlined here.

Conclusion

We have measured the nascent vibrational distribution of the CO product obtained by photolyzing 3,5-cycloheptadienone at 193, 249, and 308 nm. The measured distributions are consistent with a statistical model where the full reaction exoergicity is available for partitioning among all the products's degrees of freedom. This indicates the developing fragments are strongly coupled well into the exit channel. These findings are contrasted with our results on the dissociation dynamics of 3-cyclopentenone where the product vibrational energy distribution is determined at the transition state, i.e., the fragments are vibrationally decoupled from one another in the exit channel so that only the transition states' non-fixed energy is available to the products' vibrational modes. A mechanistically based model for the differences in energy disposal dynamics between 3,5-cycloheptadienone and 3-cyclopentenone is suggested.

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Registry No. CO, 630-08-0; 3,5-cycloheptadienone, 1121-65-9; 3-cyclopentenone, 14320-37-7.

Detection of the Prototype Phosphonium (CH_2PH_3), Sulfonium (CH_2SH_2), and Chloronium (CH_2ClH) Ylides by Neutralization–Reionization Mass Spectrometry: A Theoretical Prediction[1]

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Abstract: Ab initio molecular orbital calculations with polarized basis sets and incorporating electron correlation have been carried out on the prototype phosphonium (CH_2PH_3), sulfonium (CH_2SH_2), and chloronium (CH_2ClH) ylides, and the corresponding ylidions ($CH_2PH_3^{+\cdot}$, $CH_2SH_2^{+\cdot}$, and $CH_2ClH^{+\cdot}$). The results are discussed within the context of the detectability of reactive neutral molecules by neutralization–reionization mass spectrometry.

In a recent communication, McLafferty et al.[2] demonstrated how combination of the techniques of neutralization[3] followed by reionization[4] in a tandem mass spectrometer[5] gives rise to a powerful, new mass-spectrometric procedure: neutralization–reionization mass spectrometry (NRMS). NRMS may in particular be used to study unstable and reactive neutrals whose parent ions are stable (e.g., $CH_2{=}CHOH/CH_2{=}CHOH^{+\cdot}$). In the ideal experiment, the stable parent ion is generated uniquely and neutralized, and the neutral which is produced is reionized and characterized by using collisionally activated dissociation (CAD). Observation of a CAD spectrum which coincides with that of the parent ion demonstrates the stability of the neutral within the time frame ($\sim 10^{-6}$ s) of the NRMS experiment.

For some time now, our theoretical studies have been concerned with systems which turn out to be ideally suited for examination by the NRMS procedure, viz. stable ions whose neutral counterparts are either unstable or reactive.[6,7] In this paper we show how theory may be used to predict whether a particular neutral of this type is likely to be "detectable" by NRMS. For this to be the case, *the energy of the vertically neutralized species should be lower than that of transition structures for subsequent rearrangement or fragmentation.* We illustrate the approach with calculations on the prototype phosphonium (CH_2PH_3), sulfonium (CH_2SH_2), and chloronium (CH_2ClH) ylides.[8]

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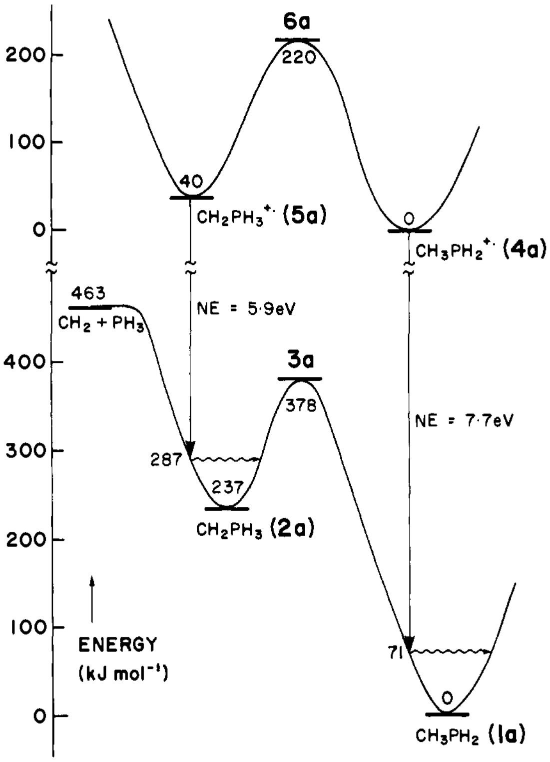

Figure 1. Schematic potential energy profile showing the production of CH_2PH_3 (**2a**) by vertical neutralization of $CH_2PH_3^{+\cdot}$ (**5a**) and possible rearrangement and fragmentation reactions.

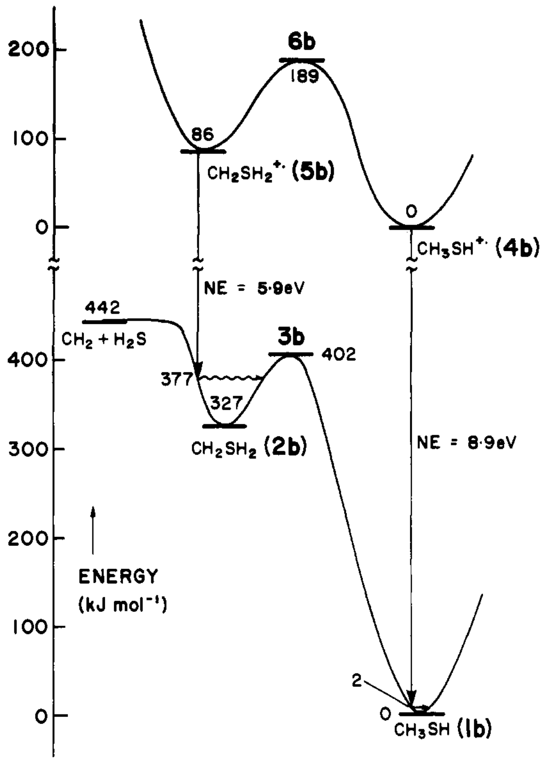

Figure 2. Schematic potential energy profile showing the production of CH_2SH_2 (**2b**) by vertical neutralization of $CH_2SH_2^{+\cdot}$ (**5b**) and possible rearrangement and fragmentation reactions.

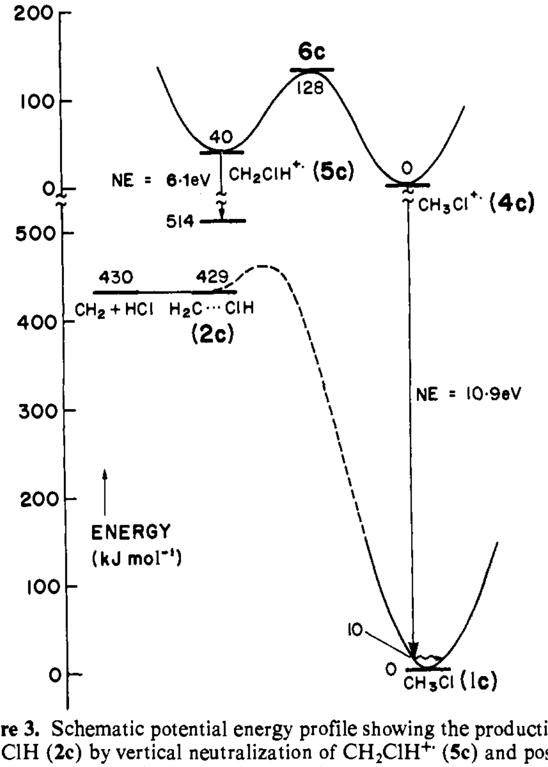

Figure 3. Schematic potential energy profile showing the production of CH_2ClH (**2c**) by vertical neutralization of $CH_2ClH^{+\cdot}$ (**5c**) and possible rearrangement and fragmentation reactions.

In recent years, we[7,9] and others[10-13] have found that the ionized forms of simple ylides such as $^{-}CH_2OH_2^{+}$ are particularly stable. Thus, for example, the methyleneoxonium radical cation, $\cdot CH_2OH_2^{+}$, lies substantially lower in energy (45 kJ mol^{-1} theoretically,[7b] 29 kJ mol^{-1} experimentally[11a,b]) than the methanol radical cation. We introduce here the term *ylidion* to describe the class of ions corresponding to such ionized ylides. The ylidions represent a particular class (charge and radical sites on adjacent centers) within the more general classification of *distonic* (from the Greek *διεστῶς* (*diestos*) and the Latin *distans* meaning *separate*) radical cations in which the charge and radical sites are separated, e.g., $\cdot CH_2CH_2OH_2^{+}$. The ylidions provide an attractive starting point for the assessment of the stability of simple ylides by means of the NRMS experiment.

Methods and Results

Standard ab initio calculations have been carried out[14] on the ylides CH_2XH (**2**), the ylidions $CH_2XH^{+\cdot}$ (**5**), the corresponding conventional isomers CH_3X (**1**) and $CH_3X^{+\cdot}$ (**4**), the transition structures (**3**, **6**) for the rearrangements **2** → **1** and **5** → **4**, and the dissociation products CH_2 (singlet) + XH and $CH_2^{+\cdot}$ + XH, for X = PH_2 (**a**), SH (**b**), and Cl (**c**). Optimized structures were derived with the split-valence-plus-d polarization 6-31G* basis set,[17] and improved relative energies were obtained with the larger 6-31G** basis set[17] and with electron correlation incorporated by using Møller–Plesset perturbation theory terminated at third

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

		X = PH_2 (**a**)		X = SH (**b**)		X = Cl (**c**)	
	no.	ΔE[b]	ΔE[c]	ΔE[b]	ΔE[c]	ΔE[b]	ΔE[c]
CH_3X	**1**	0	0	0	0	0	0
CH_2XH	**2**	244	237	334	327	458	429
TS: **2** → **1**	**3**	392	378	428	402		
CH_2 + XH		499	463	479	442	467	430
CH_3X[d]		71	71[e]	2	2[e]	10	10[e]
CH_2XH[d]		294	287[e]	384	377[e]	543	514[e]
$CH_3X^{+\cdot}$	**4**	0	0	0	0	0	0
$CH_2XH^{+\cdot}$	**5**	48	40	95	86	55	40
TS: **5** → **4**	**6**	240	220	205	189	148	128
$CH_2^{+\cdot}$ + XH		570	535	502	466	294	260
$CH_3X^{+\cdot}$[f]		65	65[e]	2	2[e]	0	0[e]
$CH_2XH^{+\cdot}$[f]		86	79[e]	136	126[e]	296	282[e]
NE($CH_3X^{+\cdot}$)[g]		7.7	7.7	8.9	8.9	10.9	10.9
NE($CH_2XH^{+\cdot}$)[g]		5.9	5.9	6.0	5.9	5.9	6.1
IE(CH_3X)[g]		9.1	9.1	9.0	9.0	11.0	11.0
IE(CH_2XH)[g]		6.8	6.8	6.9	6.9	9.3	9.5

[a] HF/6-31G* optimized structures. [b] MP3/6-31G** value from eq 1. [c] MP3/6-31G** value with zero-point vibrational correction. [d] Calculated at the optimum geometry of the ion, i.e., vertical neutralization. [e] Obtained by assuming that the excess energy resulting from geometric distortion is the same as in the vibrationless system. [f] Calculated at the optimum geometry of the neutral, i.e., vertical ionization. [g] Neutralization energies (NE) and ionization energies (IE) in eV.

order (MP3).[18] The effects of zero-point vibration have been evaluated from vibrational frequencies calculated[19] at the 3-21G(*)//3-21G(*) level.[20] Our best relative energies have been estimated by using the additivity relationship[21]

$$\Delta E(\mathrm{MP3/6\text{-}31G^{**}}) \approx \Delta E(\mathrm{MP3/6\text{-}31G^{*}}) + \Delta E(\mathrm{HF/6\text{-}31G^{**}}) - \Delta E(\mathrm{HF/6\text{-}31G^{*}}) \quad (1)$$

These values are presented in Table I, both with and without the zero-point correction. Included in Table I are the energies of CH_3X and CH_2XH at the optimum $CH_3X^{+\cdot}$ and $CH_2XH^{+\cdot}$ geometries, respectively (corresponding to vertically neutralized species), and the energies of $CH_3X^{+\cdot}$ and $CH_2XH^{+\cdot}$ at the optimum CH_3X and CH_2XH geometries, respectively (corresponding to vertically ionized species). Schematic energy profiles are displayed in Figures 1–3. Full details of structures and energies will be published in a paper dealing with more general aspects of ylides and ylidions.[22]

Discussion

The equilibrium structure for CH_2PH_3 (**2a**) is found to lie 237 kJ mol^{-1} above that of CH_3PH_2 (**1a**). Our calculations show (Table I, Figure 1) that when CH_2PH_3 (**2a**) is formed by vertical neutralization of $CH_2PH_3^{+\cdot}$ (**5a**), it has at least 50 kJ mol^{-1} of excess energy. The total amount of excess energy consists partly of the energy cost of distortion of CH_2PH_3 (**2a**) from its optimum structure to the equilibrium structure of $CH_2PH_3^{+\cdot}$ (**5a**) (amounting to 50 kJ mol^{-1}) and partly of the difference between the neutralization energy of CH_2PH_3 and the ionization energy of the metal used in the neutralization process. The latter contribution can be reduced to near zero by choosing a metal with an appropriate ionization energy. The barriers for CH_2PH_3 to rearrange to CH_3PH_2 or to dissociate to CH_2 + PH_3 are, however, substantially higher than 50 kJ mol^{-1} at 141 and 226 kJ mol^{-1}, respectively. Thus, provided a metal of appropriately high ionization energy is used in the neutralization process, the CH_2PH_3 formed should be quite long-lived and so the CAD spectrum following reionization should essentially be that of $CH_2PH_3^{+\cdot}$. If metals of lower ionization energy are used, CH_2PH_3 will be formed with larger amounts of excess energy and rearrangement and dissociation may take place to some extent. The CAD spectrum would be correspondingly modified.

Our calculated vertical neutralization energies (Table I) provide a guide as to what metal might be used in the neutralization step of the NRMS experiment, bearing in mind that the ionization energy (IE) of the metal should ideally be close to the neutralization energy (NE) of the ylidion. In practice, neutralization could occur with an energy defect, but if this were large the reaction cross section would be expected to be low. In the case of $CH_2PH_3^{+\cdot}$ (NE = 5.9 eV), Ca (IE = 6.11 eV) would produce CH_2PH_3 near threshold whereas Na (IE = 5.14 eV) would produce the ylide with significant excess energy. Neutralization of $CH_3PH_2^{+\cdot}$ (NE = 7.7 eV), on the other hand, would proceed more efficiently with Mg (IE = 7.64 eV).

When CH_2SH_2 (**2b**) is formed by vertical neutralization from $CH_2SH_2^{+\cdot}$ (**5b**), the threshold value of the excess energy is again 50 kJ mol^{-1} (Table I, Figure 2). In this case, however, barriers to rearrangement and dissociation are somewhat lower than for the corresponding phosphorus system with calculated values of 75 and 115 kJ mol^{-1}, respectively. A CAD spectrum characteristic of $CH_2SH_2^{+\cdot}$ should be observable, but contributions from the rearrangement and dissociation processes would be expected. The calculated neutralization energy for $CH_2SH_2^{+\cdot}$ (NE = 5.9 eV) is the same as for $CH_2PH_3^{+\cdot}$.

Finally, CH_2ClH (**2c**) is found to be located in a very shallow potential well, with a barrier to dissociation to CH_2 + HCl of barely 1 kJ mol^{-1} (Table I, Figure 3). The weakly bound nature of this species,[23] characterized by a long CH_2...ClH bond, has prevented us from finding a transition structure for its rearrangement to CH_3Cl (**1c**) (shown as a dashed line in Figure 3). It would seem, however, that with an excess energy of 85 kJ mol^{-1} when formed vertically from $CH_2ClH^{+\cdot}$ (**5c**), CH_2ClH should not survive the neutralization experiment but is likely to dissociate to CH_2 + HCl and/or rearrange to CH_3Cl. Accordingly, the CAD spectrum might be expected to consist of contributions from these species. The NRMS experiments performed to date on $CH_2ClH^{+\cdot}$ show both $M^{+\cdot}$ (*m/z* 52) and $HCl^{+\cdot}$ and an $M^{+\cdot}$:$HCl^{+\cdot}$ ratio which increases with increasing ionization energy of the neutralizing metal.[2] We suggest that the $M^{+\cdot}$ (*m/z* 52) ion that has been observed is $CH_3Cl^{+\cdot}$ rather than $CH_2ClH^{+\cdot}$. A definitive interpretation of the experimental results will, however, have to await further experiments[24] designed to establish, firstly, the identity of the observed $M^{+\cdot}$ (*m/z* 52) ion (i.e., $CH_2ClH^{+\cdot}$ or $CH_3Cl^{+\cdot}$) and, secondly, the origin of the $HCl^{+\cdot}$ (i.e., to distinguish ions formed from neutral fragments[25] from those formed from

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[24] See footnotes 11 and 15 of ref 2.

2c after CAD ionization). Our results strongly suggest that the observed $M^{+\cdot}$ is $CH_3Cl^{+\cdot}$ rather than $CH_2ClH^{+\cdot}$ and that the observed $HCl^{+\cdot}$ arises from fragmentation prior to CAD ionization.

Conclusions

We have shown in this paper how theory can aid in the design of NRMS experiments in two important ways. In the first place, through its ability to provide detailed potential energy surfaces, theory can suggest which systems might be suitable (and which might be unsuitable) targets for an NRMS investigation. And secondly, through its ability to predict neutralization energies, theory can suggest which metals might be most appropriate for the neutralization step of the experiment.

Our calculations predict in particular that the refined[24] NRMS experiment may provide an excellent means of establishing the stability of the prototype phosphonium ylide (CH_2PH_3). The sulfonium ylide (CH_2SH_2) should survive the NRMS experiment, but the CAD spectrum is likely to be contaminated by fragments arising from rearrangement and dissociation products of CH_2SH_2. We predict that the chloronium ylide (CH_2ClH) will dissociate and/or rearrange when formed by neutralization of $CH_2ClH^{+\cdot}$.

Acknowledgment. We are indebted to Professor F. W. McLafferty for a preprint of his paper which inspired the present study and to Professor R. F. Porter for helpful correspondence.

Registry No. **1a**, 593-54-4; **1b**, 74-93-1; **1c**, 74-87-3; **2a**, 36429-11-5; **4a**, 91391-14-9; **4b**, 53369-41-8; **4c**, 12538-71-5; **5a**, 56898-66-9; **5b**, 63933-47-1; **5c**, 81255-84-7.

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[25] The neutral fragments could in principle arise from dissociation of the neutralized parent (e.g., $CH_2ClH \rightarrow CH_2 + ClH$) or from dissociation of $CH_2ClH^{+\cdot}$ through collision with the metal vapor. We favor the latter possibility because of the large energy defect which would be involved in neutralization of $CH_2ClH^{+\cdot}$ with Hg or Zn (see text).

Interplay of Homoconjugative, Inductive, and Hyperconjugative Perturbations in 1,6:8,13-Bridged [14]Annulenes. An ESR Study of the Radical Cations

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Abstract: The radical cations of the following bridged [14]annulenes have been studied by ESR spectroscopy: 1,6:8,13-propane-1,3-diylidene[14]annulene (**1**) and its 7,14-dimethyl (**2**), 15-methyl (**3**), 17-oxo (**4**), and 17-oxo-15,16-dimethyl (**5**) derivatives, and 1,6:8,13-ethanediylidene[14]annulene (**6**) and its 15-methyl (**7**) and 15,16-dimethyl (**8**) derivatives. On passing from $\mathbf{1}^{+\cdot}$ to $\mathbf{6}^{+\cdot}$, there is a striking change in the nodal properties of the singly occupied orbital. This change has been rationalized in terms of the delicate balance of perturbations exerted by the bridging alkanediylidene group on the pair of degenerate HOMO's in the 14-membered π perimeter. Whereas for **1** homoconjugation is most effective in removing the degeneracy of the perimeter HOMO's, the energetic sequence of these MO's in **6** is dominated by inductive and hyperconjugative perturbations. Strong hyperconjugative interaction in $\mathbf{6}^{+\cdot}$ manifests itself by the large β-proton coupling constant of 2.815 mT, which is the prominent feature in the ESR spectrum of this radical cation.

The 1,6:8,13-bridged [14]annulenes[1] represent an interesting series of compounds, because the variety of the bridging alkanediylidene groups enables one to study diverse effects of such groups on the geometry and electronic structure of the 14-membered π perimeter. To this end, these compounds have been investigated by proton magnetic resonance,[2] X-ray crystallography,[3] and photoelectron spectroscopy[4] as well as by optical absorption, polarized fluorescence, and circular dichroism.[5] In particular, two of these studies[4,5] have aimed at assessing the importance of (i) distortions of the π perimeter from planarity, (ii) homoconjugative interaction between the formally nonbonded but spatially proximate bridged centers, (iii) inductive perturbation by the bridging groups, and (iv) hyperconjugation of the perimeter π orbitals with the σ orbitals of these groups. The most sensitive tool to probe the effects of (i)–(iv) on the electronic structure is ESR spectroscopy, since the nodal properties of the singly occupied orbitals enable one to determine the energetic sequence of the frontier MO's and thus to find out how their degeneracies are affected by the introduction of the bridging group.[6a] About 12 years ago, ESR studies of the radical anions of several 1,6:8,13-bridged [14]annulenes established that the singly occupied orbitals in all these species correlate with the perimeter LUMO of the *same* nodal properties.[7] This statement also holds for the radical anions of other bridged [14]annulenes in the series which have since been studied.[8] As is pointed out in the present paper, such a uniform behavior is consistent with the prediction that the perturbations, which are effective in removing the degeneracy of the perimeter LUMO's, should work in the *same* direction. Thus, although the studies of the radical anions of 1,6:8,13-bridged [14]annulenes give insight into the effect of nonplanarity on the proton coupling constants,[7,8] they are less useful for sorting out the role of individual perturbations in removing orbital degeneracy. It is also shown that the situation is more favorable in the case of the corresponding radical cations, since some of the pertur-

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