$\Delta H_f{}^{\circ}{}_{298}(H^+) = 367.2$ kcal mol^{-1} together with[39] $\Delta H_f{}^{\circ}{}_{298}$(cyclohexanone) = -54.04 kcal mol^{-1} leads to $\Delta H_f{}^{\circ}{}_{298}$(cyclohexanone enolate anion) = -55.2 ± 3 kcal mol^{-1}. We have not been able to find experimental heats of formation for 1-methoxycyclohexene and 2-methylcyclohexanone. However, they can be estimated by applying Benson's method of group equivalents:[40] $\Delta H_f{}^{\circ}{}_{298}$(1-methoxycyclohexene) = -39.7 kcal mol^{-1} and $\Delta H_f{}^{\circ}{}_{298}$(2-methylcyclohexanone) = -56.6 kcal mol^{-1}. These are likely to be reasonable estimates. The liquid phase heat of formation for 2-methylcyclohexanone is reported[39] to be -68.8 kcal mol^{-1}. If one assumes that the heat of vaporization[39] will be nearly the same as that for the isomeric cycloheptanone ($\Delta H^{\circ}{}_{vap} = 12.4$ kcal mol^{-1}), the estimated $\Delta H_f{}^{\circ}{}_{298}$(2-methylcyclohexanone) is -56.4 kcal mol^{-1}.

(38) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl.*, **6** (1977).

(39) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.

(40) S. W. Benson, "Thermochemical Kinetics", 2nd ed., John Wiley and Sons, New York, 1976.

This is quite close to Benson's estimate. Use of these heats of formation directly leads to $\Delta H^{\circ}{}_{298}(4a) = -26.9 \pm 3$ kcal mol^{-1} and $\Delta H^{\circ}{}_{298}(4b) = -43.8 \pm 3$ kcal mol^{-1}.

The methyl cation affinity (MCA) was calculated by using the following relation: MCA(cyclohexanone enolate) = $\Delta H_f{}^{\circ}{}_{298}$(cyclohexanone enolate anion) + $\Delta H_f{}^{\circ}{}_{298}(CH_3{}^+) - \Delta H_f{}^{\circ}{}_{298}$(1-methoxycyclohexene). Adoption[38] of $\Delta H_f{}^{\circ}{}_{298}(CH_3{}^+) = 264$ kcal mol^{-1} leads to MCA(cyclohexanone enolate) = 248 kcal mol^{-1}.

The thermochemistry of reaction 5 is calculated by using the heats of formation of the cyclohexanone enol radical, CH_3Br, 1-methoxycyclohexene, and bromine atom. We use[38] $\Delta H_f{}^{\circ}{}_{298}(Br) = 26.74$ kcal mol^{-1}; the heat of formation of cyclohexanone enol radical can be extracted from the EA. Zimmerman et al.[34] find EA(cyclohexanone enol radical) = 35.8 ± 1.2 kcal mol^{-1}; use of $\Delta H_f{}^{\circ}{}_{298}$(cyclohexanone enolate anion) yields $\Delta H_f{}^{\circ}{}_{298}$(cyclohexanone enol radical) = -19.4 ± 3.2 kcal mol^{-1}. The heat of reaction 5 can then be calculated as $+14.8 \pm 3.2$ kcal mol^{-1}.

Correlation of Acyl Ion Intensities with Product Enthalpies from Collisionally Activated Decomposition of Molecular Ions of Small Aliphatic Ketones

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Contribution from the Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, Research Triangle Park, North Carolina 27709. Received September 14, 1984

Abstract: Previously observed correlations of collisionally activated decomposition (CAD) fragment ion intensities of proton-bound pairs of bases with product enthalpies are extended to competitive cleavages of aliphatic ketones to acyl ions. The ratio of intensities of the acyl ions formed by CAD of the molecular ions of acetone, 2-butanone, 3-methyl-2-butanone, and 2-methyl-3-pentanone has an excellent correlation ($r = 0.997$) with the difference between the heats of formation of the sets of products.

Enthalpy differences can be predicted from fragment ion intensities when an accelerated gaseous ion decomposes after activation by collision with a thermal noble gas atom. For eq 1, the ratio of intensities of B_1H^+ and B_2H^+ in both the unimolecular mass-analyzed ion kinetic energy (MIKE) spectrum and in the collisionally activated decomposition (CAD) MIKE spectrum of $B_1HB_2{}^+$ formed in a chemical ionization (CI) source correlates with the difference between the proton affinities of B_1 and B_2.

$$B_1H^+ + B_2 \leftarrow B_1HB_2{}^+ \rightarrow B_1 + B_2H^+ \qquad (1)$$
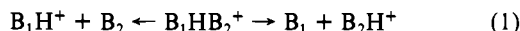
Unknown proton affinities of other bases, B_x, can, therefore, be determined from the MIKE spectrum of the proton-bound base pair $B_1HB_x{}^+$ when the proton affinity of B_1 is known.[1-3]

The slope of this kind of correlation of ion intensities has been extended to reactions in which stronger, covalent bonds are broken and to reactions in which the colliding ion has been formed by electron ionization (EI).[4] That extension required a reformulation of the supporting theory, which previously had used the concept of equivalent temperature. Although for CI ions this concept is certainly tenable,[5,6] for EI ions it has much less physical meaning. The correlation, which was observed for substituted ions related to eq 2, was not nearly as satisfactory ($r = 0.82$) as those observed in CI studies nor was the correlation of intensities of the same ions produced by unimolecular decomposition.[7] One kind of

$$C_4(C_6H_5)_4{}^+\cdot \rightarrow C_6H_5C{\equiv}CC_6H_5{}^+\cdot + C_6H_5C{\equiv}CC_6H_5 \qquad (2)$$

qualitative correlation of EI ions might have been expected, for CAD spectra often resemble EI spectra, and correlations of EI fragment ion intensities from substituted aromatic compounds with, for example, Hammett σ constants have long been known.[8,9]

On the other hand, little has been done to correlate the intensities of aliphatic fragment ions produced in an EI source.[10] Further, the proposed requirement[4] that $k(E)$ functions for competitive decompositions be sufficiently parallel that the ratio of rates does not vary significantly over the energy range of colli-

(1) McLuckey, S. A.; Cameron, D.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 1313–1317.

(2) Wright, L. G.; McLuckey, S. A.; Cooks, R. G.; Wood, K. V. *Int. J. Mass. Spectrom. Ion Phys.* **1982**, *42*, 115–124.

(3) McLuckey, S. A.; Cooks, R. G.; Fulford, J. E. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 165–174.

(4) Bursey, M. M.; Harvan, D. J.; Hass, J. R.; Becker, E. I.; Arison, B. H. *Org. Mass Spectrom.* **1984**, *19*, 160–164.

(5) Field, F. H. *J. Am. Chem. Soc.* **1969**, *91*, 1817–1839.

(6) Field, F. H. *J. Am. Chem. Soc.* **1969**, *91*, 6334–6341.

(7) Bursey, M. M.; Harvan, D. J.; Hass, J. R.; Becker, E. I.; Arison, B. H. *Org. Mass Spectrom.*, in press.

(8) McLafferty, F. W. *Anal. Chem.* **1959**, *31*, 477–478.

(9) Bursey, M. M.; McLafferty, F. W. *J. Am. Chem. Soc.* **1966**, *88*, 529–536.

(10) Bursey, M. M.; White, E. S. *Org. Mass Spectrom.* **1968**, *1*, 543–550.

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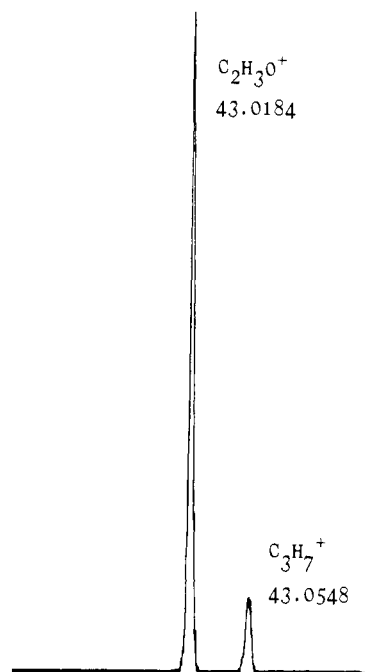
Figure 1. CAD products of nominal m/z 43 from the molecular ion of 3-methyl-2-butanone at resolution 5500.

sionally activated precursors sampled—likely a broad range—is, a priori, restrictive. Hence, correlations of CAD fragment ion intensities with product enthalpies may not be widespread in the aliphatic series. This study seeks a correlation of the logarithm of the ratio of the intensities of the two acyl ions formed by collisional activation of 7-kV aliphatic ketone molecular ions on helium, eq 3, with the thermochemistry of products. In eq 3 R_S

$$R_SCO^+ + R_L \leftarrow R_SCOR_L^+ \cdot \rightarrow R_S + R_LCO^+ \qquad (3)$$
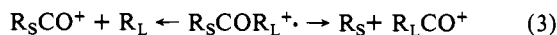
and R_L are the smaller and larger alkyl substituents on the carbonyl group, respectively.

Experimental Section

Ketones were commercial samples of the highest purity obtainable. Their mass spectra were consistent with undetectable amounts of impurities.

The mass spectrum of 3-methyl-2-butanone contains an m/z 43 current that is a mixture of $C_2H_3O^+$ and $C_3H_7^+$, and it was assumed that the intensity of the $C_2H_3O^+$ product after collisional activation could not be obtained from the intensity of the unresolved m/z 43 current recorded on a conventional MIKE (reversed Nier–Johnson) spectrometer. Specific isotopic labeling of the ketone would solve this problem but would introduce another one, the isotope effect on fragment ion intensity, which sometimes is quite large. We, therefore, addressed the problem by high resolution of the CAD products. The instrument used was a four-sector tandem mass spectrometer of BEEB geometry, the ZAB-4F (VG Analytical Ltd., Manchester, U.K.).[11] Collisions with He occurred in a cell located in the field-free region between the two electric sectors, and the last two sectors provided high resolution of the CAD products. Molecular ions of the ketones (produced by 70-eV electrons in a 200 °K source) were accelerated to 7000 V, mass-selected, and transmitted to the collision cell. Figure 1 shows the resolution of the $C_3H_7^+$ and $C_2H_3O^+$ product ions formed by collision of 3-methyl-2-butanone molecular ions with He. (The resolution of CAD products was about 5500 in this study.) Under these conditions none of the other ketone molecular ions reported showed interferences at the mass of either acyl ion.
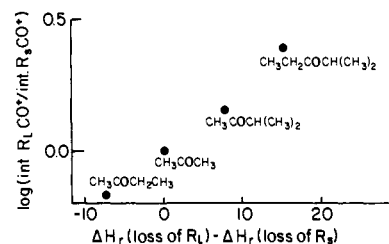
Thermochemical data were taken from a standard compilation.[12]

Results and Discussion

There are several restrictions on the number of aliphatic ketones studied. First, insufficient data were available in the literature
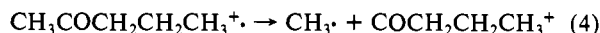
(11) Hass, J. R.; Green, B. N.; Bateman, R. H.; Bott, P. A., unpublished results.
(12) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl.* **1977**, *6*, No. 1.

Figure 2. Correlation of the logarithm of the ratios of intensities of acyl ions produced by CAD of the molecular ions of 2-butanone, acetone, 3-methyl-2-butanone, and 2-methyl-3-pentanone with differences between product enthalpies.

to produce a value of ΔH_f° for the pivaloyl ion, $(CH_3)_3CO^+$; therefore *tert*-butyl ketones were excluded from the study. Second, ketones with a β-alkyl substituent (in the n series, 2-pentanone and larger, for example) are expected from prior studies[13] to lose alkyl groups competitively from the carbonyl group and the alkyl chain, for example, as in eq 4 and 5. The major contributing

$$CH_3COCH_2CH_2CH_3^+ \cdot \rightarrow CH_3 \cdot + COCH_2CH_2CH_3^+ \qquad (4)$$

$$CH_3COCH_2CH_2CH_3^+ \cdot \rightarrow CH_3COCH_2CH_2^+ + CH_3 \cdot \qquad (5)$$

isomer in larger ions, the ion formed by loss of the terminal alkyl group from the aliphatic chain, is not observed in the compounds actually reported in this study because the $RCOCH_2^+$ structure is unstable; when R = H, it does not exist in an energy well.[14] However, ketones containing n-propyl groups and larger must be excluded from the correlation. (Again, labeled compounds solve the problem of the origin of the CH_3 lost but introduce the problem of unknown, possibly large, isotope effects.) Third, there is previous documentation of deviations from linearity both when hydrogen bonds[3] and when covalent bonds[4] break; these deviations have been ascribed to effects of increasing the degrees of freedom of the active ion[4] and to entropic effects.[3,4]

Accordingly, paucity of thermochemical data, complications in the fragmentation process, and degrees of freedom and entropic considerations reduced the number of alkyl substituents that can be safely studied to only methyl, ethyl, and iso-propyl. The entire series of usable compounds giving distinguishable points encompasses only four examples: acetone, 2-butanone, 3-methyl-2-butanone, and 2-methyl-3-pentanone. The logarithm of the intensity ratio $I(R_LCO^+)/I(R_SCO^+)$ is plotted against the quantity $[\Delta H_f^\circ(R_SCO^+) + \Delta H_f^\circ(R_L) - \Delta H_f^\circ(R_LCO^+) - \Delta H_f^\circ(R_S)]$, the difference between the enthalpies of the two sets of products of eq 3, in Figure 2. The correlation is astonishingly good in light of the quality of previous correlations[4,7] of CAD product intensities of EI ions and in light of our previous doubts about the constancy of the $k(E)$ ratios for the competitive processes, as noted above. The latter point may be reconciled with the actual result by noting that the ions are relatively small. The $k(E)$ curves for their simple dissociations should, therefore, rise sharply to limiting values. Population of energy states where the $k(E)$ values are near their limits—that is, where the $k(E)$ curves are flat and parallel—is probable.

In passing, the old rule of thumb[15] that loss of the larger alkyl group R_L is more important than loss of the smaller R_S alkyl group in the EI spectrum of R_SCOR_L can in principle be put on a quantitative basis now. The expection to this rule predicted by thermochemistry, 2-butanone, also is an exception experimentally under CAD conditions, for the point, with a negative abscissa, still falls on the correlation line. (The EI spectrum of 2-butanone actually follows the rule and violates the simple thermochemical argument; that is the m/z 43 peak is actually bigger than the m/z

(13) For the well-documented case of 2-pentanone, see: Beynon, J. H.; Caprioli, R. M.; Cooks, R. G. *Org. Mass Spectrom.* **1974**, *9*, 1–11. McAdoo, D. J.; McLafferty, F. W.; Hudson, C. E.; Parks, T. E. *Org. Mass Spectrom.* **1984**, *19*, 353–362.
(14) Nobes, R. H.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 309–314.
(15) McLafferty, F. W. "Interpretation of Mass Spectra", 3rd ed.; University Science Books: Mill Valley, CA, 1980; p 58.

57 peak in the conventional EI spectrum, and consecutive processes could occur.) In general, the quantitative basis for correlation of ion intensities with product stabilities appears to lie in the accessibility of the asympotitic portion of the $k(E)$ curve for the competitive processes studied by collisional activation. This would generally be the case for small ions; we have seen it here for ions with up to 42 degrees of freedom, and our previous studies[4,7] have shown a poorer correlation for 142–154 degrees of freedom.

Correlations of high quality between CAD product ion intensities and product enthalpies are more general than previously supposed. Their usefulness for establishing the thermochemistry of novel small ions, radicals, and molecules, produced by the fragmentation of ions generated by EI, should be exploited.

Role of the Madelung Energy in the Neutral–Ionic Phase Transition of Tetrathiafulvalene Chloranil

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Contribution from the Department of Chemistry, University of Mississippi, University, Mississippi 38677, and IBM Research Laboratory, San Jose, California 95193. Received December 14, 1983

Abstract: In order to elucidate what determines the degree of charge transfer from donor to acceptor in charge-transfer solids, we have calculated the crystalline electrostatic Madelung energy, E_M, for tetrathiafulvalene (TTF) chloranil as a function of pressure and temperature. At 300 K between 1 bar and 11 kbar, where there is a transition between Neutral and Ionic ground states, E_M becomes more negative by ~0.10 eV. This increase in binding energy suggests that the pressure dependence of the Madelung energy may be sufficiently large to drive the Neutral–Ionic phase transition at high pressures. The magnitude of $E_M = -3.8$ eV at 11 kbar is used to show that the calculated energies of the Neutral and Ionic states become approximately equal at this pressure. On the other hand, at 1 bar between 300 and 50 K, where another transition between Neutral and Ionic ground states has been found, E_M becomes more negative by only ~0.05 eV, or half as much as for the transition at high pressure. This suggests that there is an additional driving force for the Neutral–Ionic transition at low temperature (which we believe is the dimerization of the stacks). Better quantitative agreement for the transition and for the charge-transfer band energy is obtained by formally including partial charge transfer in the ground state.

Mulliken charge-transfer (CT) crystals of organic π-electron donors (D) and π-electron acceptors (A) usually form compounds with mixed stacks, in which planar donor molecules alternate with acceptors along the stack.[1-3] For this reason, these materials do not exhibit the high electrical conductivity often found in compounds which have segregated (or separate) donor stacks and acceptor stacks. For the case of mixed-stack materials, the amount of charge transferred from D to A has been calculated in the Hartree approximation by McConnell et al.[4] This simple model predicts that these compounds will be either completely neutral or completely ionic, with a sharp neutral–ionic boundary defined by

$$(I_D - A_A) + E_M = 0 \qquad (1)$$

Here I_D is the ionization potential, or energy cost of ionizing the donor, A_A is the electron affinity of the acceptor, and E_M is the electrostatic Madelung energy[5] of the ionic lattice. Thus, a poor donor/acceptor combination (with large $I_D - A_A$) is predicted to form a neutral solid, whereas an excellent D/A pair should form a solid with cations and anions. This simple model has been extended by Soos et al.[6-10] to include the effects of the Mulliken transfer integral γ between D and A along the stack. γ is usually taken to be proportional to the intermolecular overlap S. The overlap S hybridizes D and A, such that compounds previously expected to be completely neutral are only *nominally* neutral (henceforth called "Neutral"). Similarly, the ionic compounds are not fully ionic, but contain *nominally* ionic (or "Ionic") molecules. Nevertheless, there is still a sharp and well-defined boundary between Neutral and Ionic compounds. A tantalizing question has been to probe the interface or boundary between

Neutral and Ionic crystals, i.e., the region where eq 1 is almost satisfied.

In a recent experimental investigation, a large number of these compounds were systematically studied.[11] The Neutral–Ionic (N–I) boundary was identified in optical measurements of the charge-transfer band energy $h\nu_{CT}$: it was shown how compounds range from being near this boundary to being far from it. For 10 of the Neutral compounds near this boundary, it was discovered[12] that applying pressure above a certain threshold causes a distinct change in the color of the crystals. This reversible change was interpreted as a phase transition from a Neutral to an Ionic solid. In one of these materials that lies particularly close to the boundary, tetrathiafulvalene (TTF) chloranil, a similar transition could also be induced at low temperatures.[12] Most of the subsequent experimental work has focused on TTF chloranil.

(1) See, e.g.: Mulliken, R. S.; Person, W. B. "Molecular Complexes: A Lecture and Reprint Volume"; Wiley: New York, 1969.
(2) See, e.g.: Briegleb, G. "Electron-Donator-Acceptor-Komplexe"; Springer: Berlin, 1961.
(3) See, e.g.: Soos, Z. G. *Annu. Rev. Phys. Chem.* **1974**, *25*, 121.
(4) McConnell, H. M.; Hoffman, B. M.; Metzger, R. M. *Proc. Natl. Acad. Sci. U.S.A.* **1965**, *53*, 46.
(5) Metzger, R. M. In "Crystal Cohesion and Conformational Energies"; Metzger, R. M., Ed.; Springer: Berlin, Heidelberg, New York, 1981; p 80.
(6) Strebel, P. J.; Soos, Z. G. *J. Chem. Phys.* **1970**, *53*, 4077.
(7) Soos, Z. G.; Mazumdar, S. *Phys. Rev. B* **1978**, *18*, 1991.
(8) Soos, Z. G. *Chem. Phys. Lett.* **1979**, *63*, 179.
(9) Soos, Z. G.; Ducasse, L. R.; Metzger, R. M. *J. Chem. Phys.* **1982**, *77*, 3036.
(10) Bruinsma, R.; Bak, P.; Torrance, J. B. *Phys. Rev. B* **1983**, *27*, 456.
(11) Torrance, J. B.; Vazquez, J. E.; Mayerle, J. J.; Lee, V. Y. *Phys. Rev. Lett.* **1981**, *46*, 253.
(12) Torrance, J. B.; Girlando, A.; Mayerle, J. J.; Crowley, J. I.; Lee, V. Y.; Batail, P.; LaPlaca, S. J. *Phys. Rev. Lett.* **1981**, *47*, 1747.

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