been shown to undergo a thermally induced reversion to **8b** in boiling pentane (35 °C) with a half-life of ~12 h: L. E. Friedrich and G. B. Schuster, *J. Am. Chem. Soc.*, **91**, 7204 (1969); **93**, 4602 (1971).

(12) It should be noted that although the alternative product, tetramethylthiete (**7a**) (which may be formed via methyl migration in **2a**), was not observed as a volatile product, it may have been formed as a minor product and undergone polymerization before volatilization: Cf. D. C. Dittmer, P. L.-F. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111, 1116 (1972).

(13) In this respect our results appear to follow a pattern similar to that established by Shechter and Robson (*J. Am. Chem. Soc.*, **89**, 7112 (1967)) in which a sulfur atom located β to a carbene center migrates in preference to hydrogen, whereas in related compounds having a similarly located oxygen atom, oxygen migration does not show a preference over hydrogen migration. To account for their observations, the authors suggested that more ready formation of a cyclic (thiiranium) ylide (of which **1a** is a bicyclic analogue) in the former case facilitates the observed heteroatom migration.

(14) In the only other published study of the chemistry of a possible 3-heterocyclobutanylidine species, pyrolysis of the sodium salt of the *S,S*-dioxide of **3a** was found to yield tetramethylallene in 55% yield: See R. Kalish and W. H. Pirkle, *J. Am. Chem. Soc.*, **89**, 2781 (1967). In an attempt to extend this apparent cycloelimination of SO_2 to an extrusion of atomic sulfur from the 3-diazo analog of **3a** itself, Kalish (Ph.D. Dissertation, University of Illinois—Urbana, 1969) reported that treatment of the corresponding hydrazone with nickel peroxide in ether affords tetramethylallene in 1.7% yield and at least 12 other products (glpc analysis) which include 2,2,4,4-tetramethylthietanone azine (45%) along with the parent thietanone (13%) and thietanol (10%); none of the remaining products, formed in yields ranging from ca. 0.2 to 4.5% each, was identified.

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The Temperature Dependence of an Electron Impact Induced Stereoselective Rearrangement Reaction

Sir:

In spite of the enormous energies utilized in the ionization process, rearrangement reactions occurring from organic molecular ions in mass spectrometers exhibit remarkable stereosensitivity to energetically small conformational differences.[1] Moreover, intramolecular transfer of diastereotopic hydrogens in parallel rearrangement reactions of chiral substrates in mass spectrometers and in solution actually show *quantitatively* similar stereoselectivities.[2] The question immediately arises as to the source of this similarity. The reacting molecules in solution are subject to a Maxwell-Boltzmann energy distribution defined by their temperature. On the contrary, in the mass spectrometer the molecular ions are not only of uncertain energy distribution because of their mode of formation by electron impact, but as well the temperature cannot be experimentally defined because of the absence of intermolecular or wall collisions for the detected ions.[3]

The source of this kinetic similarity[2] may be understood by a few simple considerations centered around the quasi-equilibrium theory of mass spectrometry.[4] The theory predicts, and experiments bear out, that rearrangement reactions in mass spectrometers occur from molecular ions of the lowest internal energies.[5] Photoelectron spectroscopy demonstrates that in molecules with nonbonding electrons these lowest internal energy ions, in focus here, are produced by removal of an electron from these nonbonding orbitals and furthermore that such ionization gives rise to discrete and relatively narrow bands often separated by an energy space from the broader bands involving higher energy ionization of bonding electrons.[6] As has been pointed out by Turner[7] such promotion of nonbonding electrons will produce an ionized state which within reasonable approximation will have the same bonding parameters as the neutral precursor. This is a key point with regard to our inquiry because it follows from the Franck-Condon principle that such a circumstance of equivalent potential surfaces for the ion and its neutral precursor will lead to producing the ionized molecule with the same vibrational and rotational energy as the neutral.[7,8] In other words, the temperature of the ion produced by removal of a nonbonding electron, within the limits of the above approximations, will be the same as the temperature of the neutral from which it is formed.[9] It thereby becomes clear why quantitatively similar rearrangement stereoselectivities[2] are observed in solution and in mass spectrometers. We can, though, go a step further.

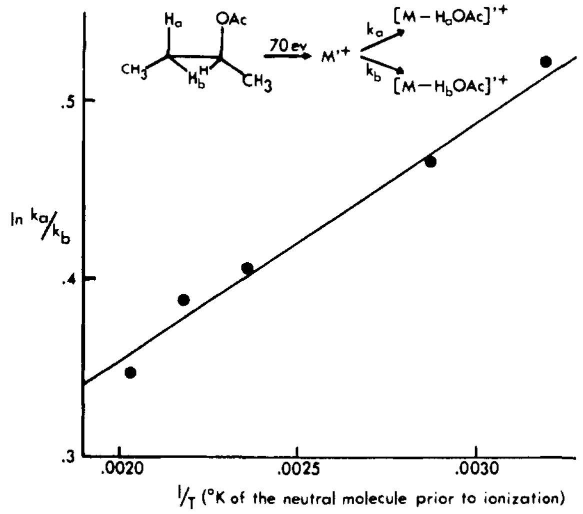

Figure 1. Measured on an MS-902 mass spectrometer at 70 eV beam energy. The construction of this instrument allows varying in consort the temperature of the inlet, ion chamber, and source walls. The temperature is accurate to ±2 °C. The experiments were conducted four times over a period of 6 months and gave the same line within experimental error. Each experiment consisted of at least five measurements at each temperature of 2-butylacetate and the two deuterated diastereomers necessary to calculate k_a/k_b.[2] The data were handled by a computer program written here which yielded the stereoselectivities and the accuracy. Each point was calculated to 95% confidence (2σ) and then used to generate the linear least-squares line shown. The line has a correlation coefficient of 0.991. Another experiment varying only the ion chamber temperature and leaving the inlet system at ambient temperature gave the same line as above with the lowered correlation coefficient of 0.968. The elimination of acetic acid is known not to be pyrolytic under these conditions.[12] The experimental data here show no time dependency at the temperatures reported and as well we have subjected 2-butylacetate to gas chromotography on steel columns and throughout this temperature range there is no evidence for pyrolysis.

If the temperature of the neutral is an accurate measure of the immeasurable temperature of the ions produced it would follow that the rearrangement rate constant for the electron impact induced reaction should depend on the temperature of the neutral precursor in the form of the Arrhenius expression. The precision of the Arrhenius dependency would moreover constitute a measure of the assumptions leading to the prediction of temperature equivalence in the ionization process producing the rearranging ions. Because a stereoselectivity involves a rate ratio which cancels out temperature dependent instrumental parameters[10] and also obviates the otherwise extreme difficulty of measuring an absolute rate constant in a mass spectrometer, we were placed in a position to test for Arrhenius temperature dependency.[11] The reaction chosen for this purpose was the stereoselective rearrangement elimination of acetic acid from electron impact produced 2-butylacetate cation radical.[2] Figure 1 shows this process as well as a plot of the stereoselectivity (k_a/k_b) as a function of the temperature of the precursor neutral.

The Arrhenius equation may be derived from Boltzmann's law[13] and thus the clear Arrhenius dependency exhibited in Figure 1 is strong evidence that the rearranging molecular

Table I[a]

β^- (eV)	$\Delta\Delta$ Energy of activation (cal mol^{-1})[c]	Ratio of preexponential factors[d]
70	264 ± 43	1.08 ± 0.06
15[b]	282 ± 22	1.02 ± 0.03

[a] The errors (±) are presented within two standard deviations (2σ). See footnote to Figure 1. [b] 15 eV is the lowest nominal beam voltage on the mass spectrometer (MS − 902) which would yield accurate data. [c] Calculated from the line slope which equals $\Delta\Delta E_{\mathrm{act}}/RT$. [d] Calculated by extrapolation of the line to temperature equals infinity.

cation radicals are in an at least approximate Maxwell-Boltzmann energy array defined by each temperature along the abscissa. This is precisely in line with the arguments made (vide supra) and can be further supported by the data presented in Table I which give the slope and, as well, the intercept at infinite temperature, for the line in Figure 1 and for an equivalent experiment conducted at low beam energy (15 eV).

There are two expectations correlative to the ideas discussed here. First, the exact temperature dependency should be independent of beam energy if only the lowest energy ions are contributing to the rearrangements under observation. Second, the ratio of preexponential factors for two reactions differing only in abstraction of diastereotopic hydrogens (H_a or H_b) should be unity. Inspection of Table I shows that the experiments yield exactly these results. Moreover, in a further experimental test, we have determined the appearance minus ionization potentials for the lowest energy fragmentations of the 2-butylacetate cation radical. Loss of acetic acid, as demanded by the current proposal, is lowest (A.P. − I.P. equals 0.3 ± 0.05 eV) with cleavage loss of methyl and ethyl next highest by another 0.3 eV.[14,15]

In conclusion, therefore, persuasive experimental evidence is presented for the theoretically justifiable proposal that rearranging molecular ions in mass spectrometers[16] when produced by ionization of nonbonding electrons maintain a close or perhaps exact correspondence to the thermal energy, that is, the temperature, of their precursor neutrals. Put in another way, the electron beam, by simply ionizing without depositing energy, converts the molecules investigated here to a highly reactive state, charged radicals, rather than to the highly excited state which might be imagined.

Clearly, the kind of experiment carried out here not only further firms the connection between mass spectrometry and thermal free radical chemistry[2] but as well offers the possibility of a quantitative conformational analysis on charged *free* radicals reacting in the fascinating nonenvironment of molecular isolation.[17]

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(14) In line with this, the percent of total ionization of loss of acetic acid is increased by three times in going from 70 to 15 eV.

(15) We are grateful to J. F. Litton and R. G. Cooks (Purdue) for making these measurements for us. Details will be presented in the full paper.

(16) A referee has correctly pointed out that rearrangement reactions manifesting higher energies of activation may occur from ions which *are* thermally excited by the electron impact. The latter processes would not be expected to show the temperature dependence reported. This would especially be so if the next higher cleavage process occurred with a greater energy spread than is present here (0.3 eV). We predict that other eliminations of HX beside HOAc (e.g., HOH, HCl) will show the dependency found here. We are testing these limits now.

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