is necessary to consider the entropy changes associated with the proton transfer. For *most* ion/molecule equilibria, ΔS may be approximated by ΔS_{rot}, the rotational energy difference due to changes in symmetry numbers.[8,21] It has been assumed for methylketene that protonation occurs on the carbon atom adjacent to the methyl group. If this is indeed the case, reaction 21 is accompanied by no changes in either external or internal symmetry numbers; thus ΔS_{rot} is 0 and the reaction is 6.5 kJ mol^{-1} exothermic. This leads to a proton affinity for methylketene of 845 ± 3 kJ mol^{-1}, some 25 kJ mol^{-1} higher than the proton affinity of ketene.

Equilibrium measurements have been made in this laboratory on several two-component systems wherein at least one of the components was an aliphatic alcohol; methanol, ethanol, 2-propanol, and 2-butanol together with formic acid, dimethyl ether, and ethyl acetate were investigated. The values of $\Delta G°$ obtained for each two-component system were in good agreement with reported values.[10] In addition to the above studies, quistor resonance ejection has been used to establish the existence of equilibrium in the carbon dioxide-methane system, and is currently being used in the study of equilibria involving negative ions.

The gas temperature is measured by two methods, though in separate experiments. Firstly, the reactant gases are assumed to be in thermal equilibrium with the body of the quistor, and the temperature of the quistor is determined with a thermocouple in contact with an end-cap electrode. Secondly, the temperature of nitrogen in the quistor is calculated from the observed rotational distribution of the nitrogen first negative system emission in the vicinity of 391 nm.[22] There is good agreement between the two methods.

Several attempts have been made to determine ion kinetic energies within the quistor as a knowledge of ion energies is essential to the study of chemical processes by this technique.[23] A distinction must be made between primary ions which are formed initially throughout the effective reactor volume and secondary ions formed in subsequent ion/molecule reactions. Primary ion kinetic energies in collision-free systems[24] and secondary ion kinetic energies pertaining after several collisions[25] have been calculated. There is good agreement among the estimates of mean primary ion energies in collision-free systems. Simulation studies[25] indicate that, although a fraction of secondary ions may possess several electronvolts of kinetic energy, rapid energy dissipation is effected in the first 6–10 collisions so that after 15 collisions the mean ion energy is ≪1 eV. Several well-characterized chemical systems have been examined by quadrupole ion storage mass spectrometry[26] and rate constants have been obtained in good agreement with literature values. The observed rotational temperature of the ions obtained in the spectroscopic study of the nitrogen first negative system referred to above should coincide with the temperature of neutrals within the quistor as the number of collisions required to equilibrate rotation with translation is small (approximately five to ten). The rotational temperature is within 20 °C of that obtained with the thermocouple and less than 40 °C above room temperature. Thus it may be concluded that the ion rotational and neutral translational energies are equilibrated and thermal. If the ions were kinetically heated by the rf field, one might expect to see some rotational perturbation in the emission spectrum, even though the lifetime of the (0,0) transition of the nitrogen first negative system ($\sim 8 \times 10^{-8}$ s[27]) is short with respect to the periodicity of the rf potential applied to the quistor. No perturbations were observed in the 21 rotational levels monitored.

The conclusion of these studies is that a rapid diminution of primary ion kinetic energy occurs during the initial ~100 μs of storage at $\sim 10^{-2}$ Pa, and is accompanied by migration of thermalized secondary ions toward the center of the quistor. Thus one may expect to observe some manifestation of translationally "hot" ions initially and, subsequently, reactions of thermalized ions at longer storage times.

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Crystal and Molecular Structure of 1,4,7-Trithiacyclononane

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Abstract: The crystal and molecular structure of 1,4,7-trithiacyclononane has been determined from a single-crystal X-ray study. The compound crystallizes in the rhombohedral space group $R3c$ with six molecules per unit cell of dimensions (hexagonal axes) $a = b = 12.584$ (3), $c = 9.209$ (2) Å. The observed and calculated densities are 1.41 (1) and 1.42 g cm^{-3}, respectively. Full-matrix least-squares refinement using 252 unique reflections having $4° \le 2\theta \le 50°$ and $I \ge 3\sigma(I)$ converged at $R = 0.0217$ and $R_w = 0.0285$. The compound exists, in the crystalline state, in the C_3 conformation with the sulfur atoms endodentate. The transannular S–S distance is 3.45 Å.

The conformation adopted by all of the crown thioethers[1] as yet studied by X-ray crystallographic methods (1,4,7-trithio(12-crown-4),[2] 1,4,8,11-tetrathio(14-crown-4),[3] 1,4-dithio(15-crown-5),[2] and 1,10-dithio(18-crown-6))[2] is one in which all of the sulfur

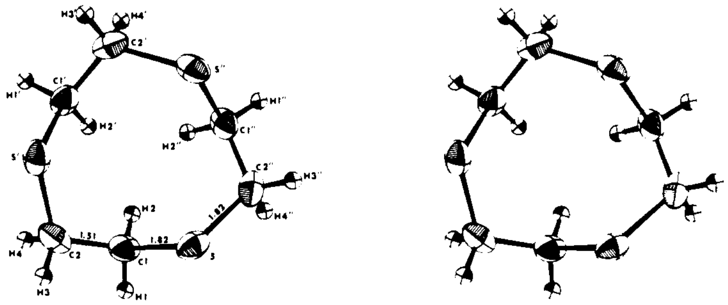

Figure 1. ORTEP[13] stereoview of 1,4,7-trithiacyclononane along the C_3 axis. The hydrogen atoms have been assigned arbitrary thermal parameters. Thermal ellipsoids are drawn to enclose 50% of the probability distribution.

atoms are directed out of the cavity (exodentate). In contrast to these results, X-ray crystallographic analysis of 1,4,7-trithio(9-crown-3) (1,4,7-trithiacyclononane), as outlined below, reveals that this molecule assumes the [333][4] conformation (C_3 symmetry) shown in Figure 1 in which the sulfur atoms are directed toward the center of the ring (endodentate). This conformation is also different from that adopted by the oxygen analogue 1,4,7-trioxacyclononane which, in solution and in the solid, as determined by ^{13}C NMR and IR spectroscopy, has an unsymmetrical [234] conformation.[5]

The compound crystallizes in the rhombohedral space group *R3c* with six molecules per unit cell of dimensions (hexagonal axes) $a = b = 12.584$ (3), $c = 9.209$ (2) Å. The observed and calculated densities are 1.41 (1) and 1.42 g cm^{-3}, respectively. A θ–2θ scan over the range $4° \leq 2\theta \leq 50°$ was used to collect a total of 298 unique reflections. Of these, 252 having $I \geq 3\sigma(I)$ were used in the solution and refinement of the structure. Examination of the collected data set indicated a rhombohedral lattice, but did not unambiguously define the space group. The structure was solved by the heavy-atom method. The space group was determined and the position of the sulfur atom located from a three-dimensional Patterson map. The structural parameters have been refined to convergence ($R = 0.0217$ and $R_w = 0.0285$).

A stereoview of the molecule viewed down its C_3 axis is shown in Figure 1 along with the labeling scheme. The bond lengths with their estimated standard deviations in parentheses for the nonhydrogen atoms are S–C(1), 1.820 (5); S–C(2)″, 1.823 (5); C(1)–C(2), 1.510 (6) Å. The bond angles with their estimated standard deviations in parentheses for the nonhydrogen atoms are C(1)–S–C(2)″, 102.8 (3); S–C(1)–C(2), 113.0 (4); C(1)–C(2)–S′, 117.0 (4)°. The torsional angles for the nonhydrogen atoms are C(2)″–S–C(1)–C(2), −131.1; S–C(1)–C(2)–S′, 58.5; C(1)–C(2)–S–C(1)′, 55.1°. The transannular S–S distance is 3.451 (2) Å, which is less than the sum of their van der Waals radii.[6]

The two especially interesting features of the structure of 1,4,7-trithiacyclononane revealed by this study are that it adopts a [333][4] or TBC[7] conformation and the sulfur atoms are endodentate. The D_3 [333] conformation is found by NMR spectroscopic analysis[8] to be the lowest energy conformer of cyclononane in agreement with calculations.[4,7,9] However, as already pointed out, the unsymmetrical [234] conformation is adopted by 1,4,7-trioxacyclononane[5] and force-field calculations find an unsymmetrical C_1 conformer to be the most stable conformation of cyclononasulfur.[10]

The fact that the sulfur atoms are endodentate in 1,4,7-trithiacyclononane may have important consequences for metal binding of this tridentate ligand. It has been suggested[11,12] that for first-row transition metals to coordinate exodentate ligands the metal initially attacks a sulfur atom of the more accessible exodentate conformer. Rearrangement then probably must occur to the endodentate conformation before a second sulfur atom coordinates. With an endodentate ligand such as 1,4,7-trithiacyclononane, an intervening conformational change is unnecessary.

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Supplementary Material Available: A table of final atomic parameters and a listing of observed structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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(1) The systematic names of the crown thioethers listed are 1,4,7-trithia-10-oxacyclododecane, 1,4,8,11-tetrathiacyclotetradecane, 1,4-dithia-7,10,13-trioxacyclopentadecane, and 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane, respectively.

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(14) **Note Added in Proof.** The X-ray structure for 1,4,7-trithiacyclononane has recently been independently solved (V. B. Pett, Ph.D. Dissertation, Wayne State University, 1979) and these results are in agreement with ours.