PRINCIPAL PROCESSES IN THE RADIOLYSIS OF GASES WITH
FISSION RECOILS AND GAMMA RAYS

MASTER

Annual Progress Report
for the Period October 16, 1979 - September 15, 1980

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

G. G. Meisels

Department of Chemistry

University of Nebraska - Lincoln

Lincoln, Nebraska 68588

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

October 1980

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Prepared for

THE U.S. DEPARTMENT OF ENERGY

DE-AS02-76-ERO-2567

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

SUMMARY AND HIGHLIGHTS

1. High resolution mass spectrometry and threshold photoelectron-coincident photoion mass spectrometry (TPE-CPI-MS) of propane-2- C^{13} showed that skeletal isomerization in propane ions precedes to a significant extent the fragmentation of that ion to ethylene ion and methane. This is the smallest hydrocarbon for which such rearrangement has been observed.

2. Methylnitrite ion was found to be exceptional in its fragmentation near threshold; TPE-CPI-MS and collision induced dissociation investigations on an MS-50-TA triple sector analyzer clearly indicate that the products NO^+ and CH_3O^+ , which could in principle arise by simple bond cleavage, are not competitive and must therefore arise from different, non-interconverting electronic states of the parent ion. Moreover, the long lifetime with respect to the second process cannot be interpreted on the basis of an energy randomized intermediate and must therefore involve a crossing of electronic states.

3. Electron range and energy loss measurements for 50 to 500 eV electrons have been made by following the formation of ions as a function of depth or penetration into the high pressure ion source (1 to 3 torr) of a mass spectrometer. Ranges within which 97% of total ionization occurs were measured for the rare gases and nitrogen.

4. A complete reanalysis of spectroscopic and equilibrium data concerning the Kr - CO and Xe - O_2 systems revealed substantial disagreement even when equilibrium measurements are made under the most carefully controlled experimental conditions. The discrepancy is ascribed to

difficulties in establishing accurately concentrations and true equilibrium conditions in high pressure ion sources.

5. Isomerization of nitromethane ion to methylnitrite ion appears to be controlled by electronic state correlation. While highly exothermic even at threshold for parent ion formation of nitromethane, dissociation and presumably isomerization to methylnitrite ion occur only from the upper, $2A''$ state of nitromethane ion, which correlates approximately with the $2A''$ state of methylnitrite ion.

I. COMPETITION BETWEEN ISOMERIZATION AND DISSOCIATION OF GASEOUS IONS

The factors controlling the degree to which ions retain the identity of their precursors have been the subject of considerable interest and activity for some time (1). Ions of the same elemental composition frequently show different collisional activation spectra, depending on the neutral precursor from which they are formed. The mass spectra produced by the impact of 70 eV electrons, as commonly used in analytical applications, show that the spectra of isomers such as the four butenes, methylcyclopropane and cyclobutane differ substantially in spite of the equality of thermodynamic properties such as onset of the lowest fragmentation pathway referred to a common internal energy scale. Interpretation of such observations usually relies upon differences in energy deposition functions and heats of formation of the ion initially formed by electron impact or other means (2,3). This mechanism almost certainly accounts for the differences in the mass spectra of the butenes.

The matter is not so clear for other ions. For example, a number of even-electron ions appear to have different structures as inferred from different heats of formation and different collision induced dissociation spectra (1,4). If this interpretation is correct, barriers towards isomerization must exist, and much speculation has appeared concerning their magnitudes and origins. We have investigated isomerization processes for a number of years, and believe that some of the information we have obtained recently indicates that we are headed towards a general overview. While the following discussion is by no means complete as yet, it presents some of the views we are developing.

It is necessary to note that some evidence on ion structure cannot distinguish between the energy content of an ion and its structure. For example, if a given ion structure can be reached from another only via a transition state which requires excess energy, that excess energy will remain in the ion because it is, in low pressure ion sources, an isolated system which cannot transfer energy to other species. Its behavior will thus differ from that of ion prepared by a different pathway from a different precursor by a low-energy path.

Overall, we can identify two basic mechanisms which control apparent retention of ion structure in contrast to isomerization to the most stable structure. We present these factors with examples of each type of behavior where possible.

1. KINETIC CONTROL. In this class of isomerizations, the degree to which randomization competes with fragmentation depends on the relative thresholds E_i and E_d for isomerization and dissociation, respectively, and on the nature of the transition state. The latter may be loose or tight, which affects the dependence of the rate constants k_i and k_d on energy E . We now subclassify these reactions further. We designate the transition state for isomerization as T_i and that for dissociation as T_d , with the parenthetical notations t indicating tight and l indicating loose. The rate constants for loose transition states rise more rapidly with energy than tight ones, and level off at higher values at high energies.

A.a. $E_i < E_d$, $T_i(l)$, $T_d(l)$. This isomerization is always rapid in the region of the first dissociation onset. When breakdown graphs are expressed relative to the ground state energy of the most stable isomer, they are identical. This mechanism applies to many hydrogen atom or

intermolecular hydride transfer reactions, particularly in olefins, which are often responsible for hydrogen/deuterium exchange and limit the utility of deuterium labelling as a probe of fragmentation mechanisms.

A.b. $E_i < E_d$, $T_i(t)$, $T_d(l)$. This is probably the most common and best understood mechanism. Isomerization frequently involves ring structures and therefore tight transition states while simple bond cleavage is loose. This mechanism predicts isomerization to be important near fragmentation onset but to decrease in importance as internal energy is increased. It applies for the four butene isomers and to methylcyclopropane and cyclobutane in the energy range to 2.6 eV above the 2-butene ion structure. Since the fragmentation onset occurs only at 2.25 eV, the energy range over which this mechanism applies is very narrow indeed.

A.c. $E_i < E_d$, $T_i(t)$, $T_d(t)$. This mechanism is probably applicable for the isomerization of small cyclic hydrocarbon structures. The dependence of the rate constant on energy for both processes is quite similar, but the two curves are offset with respect to each other.

For cyclobutane and methylcyclopropane as shown by us last year, the breakdown graph differs from that of the butenes at energies in excess above 2.6 eV, notably through the production of relatively much larger amounts of ethylene ion (Figure 1). This reflects the ability of the cyclic structures to dissociate directly from the original cyclic configuration through a new transition state which is not accessible to the olefinic structures. This fragmentation rapidly becomes competitive with the isomerization to the olefinic structure but does not take over entirely even when the energy is raised considerably. The two processes of isomerization and dissociation remain competitive, and one may estimate roughly that the rate of the direct fragmentation pathway is negligible at about 2.6 eV internal energy, but becomes increasingly competitive

until it reaches about 5% of the isomerization rate for methylcyclopropane at 3.8 eV internal energy with respect to the 2-butene ion structure.

For cyclobutane, the effect is even more pronounced and indicates that, at 3.4 eV, the rate of the direct fragmentation is about 10% that of the isomerization pathway. These conclusions are based primarily on a comparison of the relative extent to which ethylene ion is formed from the C_4H_8 isomers. (It should be noted in passing that such an analysis requires reliable breakdown graphs free of the effects of coincidences associated with energetic electrons. The breakdown graphs reported here have been corrected for these by using the methodology developed in our laboratories about a year ago (5).)

A.d. $E_i < E_d$, $T_i(l)$, $T_d(t)$. Similar to A.a., isomerization and randomization are expected to precede fragmentation at all energies; there are no known examples at this time.

B.a. $E_i > E_d$, $T_i(l)$, $T_d(l)$. Isomerization would become competitive only at relatively high internal energies when both rate constants have levelled off unless E_i and E_d are very nearly the same; no examples are known.

B.b. $E_i > E_d$, $T_i(t)$, $T_d(l)$. Isomerization never becomes competitive.

B.c. $E_i > E_d$, $T_i(t)$, $T_d(t)$. Normally isomerization should become competitive only at high energies when both rate constants have begun to level off. However, when E_i and E_d are very close, the two rate constant vs. energy curves may be expected to parallel each other closely, and relatively little change in the ratio of k_i/k_d may be evident throughout the accessible energy range. This process was not anticipated, but an example appears to be the fragmentation of the propane molecular ion to ethylene ion and methane

It is normally assumed that this process occurs predominantly via an accompanying 1,3 hydride shift to provide the fourth hydrogen atom for a terminal methyl group, with a smaller contribution of a 1,2 shift (6), however recent photoionization measurements on $\text{CH}_3\text{CH}_2\text{CH}_3$ have also shown about 6 to 7% of what appears to be a double hydrogen shift or elimination of the central carbon with hydrogen atom transfer from the terminal methyl groups to the central methylene group. We have investigated $\text{CH}_3\text{C}^*\text{H}_2\text{CH}_3$ where the star indicates the C-13 label, both using high resolution mass spectrometry and TPE-CPI-MS. We observed that $11 \pm 2\%$ of the methane loss at internal energies from 0.75 to 2.05 eV involves the central carbon regardless of energy. Since the onset of fragmentation is at an internal energy of ca. 0.72 eV, we conclude that the transition states for isomerization and fragmentation must be very nearly the same, and that the energy barriers must also be very nearly identical, with the barrier for isomerization possibly a little higher because metastable fragmentation studies, also performed on the MS-50 high resolution mass spectrometer, indicate that only ca. 2% of the fragmentation events involve the central carbon. However, such inferences on the basis of metastable intensities are somewhat uncertain because factors other than the competitive processes influence the relative abundances of the two ion products.

B.d. $E_i > E_d$, $T_i(1)$, $T_d(t)$. Here one would expect that isomerization does not take place near fragmentation onset, but that it begins to set on shortly above the threshold for isomerization E_i , and that it should be much faster than dissociation at higher energies.

2. ELECTRONIC STATE CONTROL. The preceding mechanisms are based on the assumption that the ground electronic states of all isomeric configurations are mutually accessible, that is, correlate with each other. This is not always the case. During the past year we have learned that the nitromethane ion - methylnitrite system is an unusual one; the dominant product from methylnitrite ion, in its ground state the more stable structure by about 0.4 eV, is NO^+ at higher internal energies, while CH_3O^+ is the most intense ion near onset. There is also considerable evidence (see section II) that methylnitrite ion gives the latter product only from an electronic state of the ion not accessible from the ground state. CH_3NO_2^+ does not give products up to 0.6 eV above ionization threshold, some 1.0 eV above the thermodynamic dissociation threshold. We postulate that nitromethane ion cannot reach the methylnitrite structure (or yield fragment ions) from ground, $2A'$, electronic state, but that the upper, $2A''$, state correlates to the same state of the methylnitrite ion, and that dissociation follows after isomerization. This conclusion is not yet on a very firm foundation.

3. TRANSITION STATE CONTROL. This mechanism is really a false isomerization. It corresponds to a peculiarity of the transition state which is degenerate and may fragment in two directions equal but for a label on one of them. No examples are known.

II. NON-INTERCONVERSION OF ELECTRONIC STATES BEFORE ION FRAGMENTATION

The widely accepted statistical theory of mass spectra (quasi-equilibrium theory or QET) was originally based on the assumption that molecular ions are formed in a distribution of electronically and vibrationally excited states which convert rapidly to vibrationally excited states of the ground electronic state of the ion, from which fragmentation occurs subsequently through a series of consecutive and competitive fragmentation processes from an energy randomized intermediate. (for a recent review, see reference 4) Numerous tests of the basic assumptions have been made, with initial attention paid to appropriate description of the fragmentation process itself, and later to the seeking of evidence on the generality of the dominance of the radiationless transitions leading to the ground electronic state, and on the statistical nature of the fragmentation process.

It is generally correct that electronic states convert to the ground state, and no compelling proof that this is not the case has been offered in the past for any system. This is surprising because such specific state correlated reactions are certainly well known for neutral species; one only has to think about Woodward-Hoffman rules as an example. The findings to date suggest that large molecular ions may be unique in the sense that the electron vacancy creates conditions which allow the normal state correlation rules to break down, that is, to decrease the "forbiddenness" of reaction pathways. It is partly for this reason that so much effort has been expended on searches for non-adherence to QET. Our own work has led to what may be the first example of such an exception to the basic assumptions of the theory (8).

The fragmentation of methylnitrite ion is characterized by the formation of CH_3O^+ ion over a very narrow energy range, followed rapidly by the formation of NO^+ , an ion which becomes virtually the only major species within less than 0.7 eV above fragmentation onset. (details are given in reference 8, a copy of which is attached.) The most remarkable feature is the difference in lifetimes with which these two ions are produced at the same energy; that of CH_3O^+ occurs with a halflife on the order of 5 microseconds, while that of NO^+ takes place within less than 0.7 microseconds. This is not possible if the dissociation occurs from a common precursor. Similarly, the collisional activation spectrum shows a strong peak for NO^+ formation from the parent ion, but none for the formation of the other product. This is easily understood in terms of the long lifetime of the process leading to CH_3O^+ , which is slower than the detection time of dissociated products before entry into the last electrostatic sector of the triple analyzer spectrometer.

While the different lifetimes indicate clearly that the precursors cannot be the same, the long lifetime of the first process is not consistent with QET also. For a small molecule, the rate constant should increase rapidly with energy so that the energy envelope within which lifetimes are large enough to be detected is so narrow that it should not be detectable. This observation, confirmed by the collision induced dissociation results, indicates that the dissociation must be governed by a surface crossing. Because the electronic states of the neutral CH_3O are extremely complex, it is not possible at this time to associate the reaction pathways clearly with unique states. We have measured the photoelectron spectrum of methylnitrite, however, it is too broad to be very helpful and contains, near onset, clearly a substantial number of unresolved states.

Another possible example is the fragmentation of C_2F_6 , which has been reported to fragment from an isolated electronic state (7). We have investigated this molecule using collision induced dissociation methodology but results are not conclusive. While it was possible to show that the product ion CF_3^+ arises from $C_2F_5^+$ in a secondary mechanism, this does not establish that it is not formed from the parent ion. This would be necessary to prove that separate electronic states are not involved.

III. IONIC EQUILIBRIA IN THE GAS PHASE

Last year we reported careful measurements of the ionic equilibria involving the reactions

and it appeared that the results we had obtained were in good agreement with those which one may calculate from basic spectroscopic information. Since that time, new sets of measurements of the ionization potential of oxygen, which appear to be quite reliable, were brought to our attention. These differ sufficiently from the old ones to result in a substantial disagreement between the values obtained a-priori from spectroscopic, single-species measurements combined with principles of statistical thermodynamics, and those obtained in bulk equilibrium measurements. This must be a result of experimental artifacts, and we have therefore sought their cause because thermodynamic measurements in high pressure ion sources and in ion cyclotron mass spectrometers have become wide spread, and an understanding of experimental difficulties is essential if one is to have great faith in the thermodynamic quantities derived on the basis of these measurements.

While we have expended considerable effort on this problem, we have relatively little progress to report. We are examining every possible correction which may be necessary to convert measured ion current ratios to equilibrium constants; these include discrimination effects, multiplier gain, lack of thermalization and a number of others. Results have changed somewhat but have shown an inconsistency which is relatively small, but sufficient to make it uncertain just how well one can really

measure equilibrium constants and their temperature dependence using high pressure ion sources. Further work is in progress in an attempt to eliminate errors which may be introduced by normally mundane factors, such as gas composition, pressure control, effects external to the ion source, etc.

IV. RANGE OF 100 TO 500 eV ELECTRONS

Last year we showed that high pressure mass spectrometry could be used to estimate the linear ionization rates and ranges of electrons of relatively low energy. We have extended our measurements to include all the rare gases and nitrogen (figure 3).

V. INSTRUMENTATION

The modification of the TPE-CPI instrument to allow for the study of collision reactions was not undertaken because of the exciting new information obtained on unimolecular processes.

During the past year, a high resolution (triple sector) mass spectrometer for the study of collision induced processes became available as a result of the Regional Facility in Mass Spectrometry at the University of Nebraska established by the National Science Foundation. We have used this instrument as reported above, and have also attempted to improve its energy resolution; we were successful in doing so from 1 eV to ca. 0.3 eV but this is not sufficient to investigate relative energy deposition efficiencies as planned originally.

VI. LITERATURE CITED

1. D. H. Williams and I. Howe, "Principles of Organic Mass Spectrometry", McGraw Hill, London (1972); D. H. Williams in "Advances in Mass Spectrometry", Vol. 7, Heyden, London (1977); also see J. T. Bursey, M. M. Bursey and D. G. I. Kingston, Chem. Reviews 73, 191 (1973).
2. T. Baer, in "Advances in Mass Spectrometry", Vol. 7, Heyden, London (1977).
3. G. G. Meisels, C. T. Chen, B. G. Giessner and R. H. Emmel, J. Chem. Phys. 56, 793 (1972).
4. K. Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Verlag Chemie, Weinheim-New York (1978).
5. T. Hsieh, J. P. Gilman, M. J. Weiss, G. G. Meisels and P. M. Hierl, Int. J. Mass Spectrom. and Ion Physics, in press.
6. M. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, ed.; Interscience, New York (1968).
7. M. G. Inghram, G. R. Hanson and R. Stockbauer, Int. J. Mass Spectrom. and Ion Physics 33, 253 (1980).
8. G. G. Meisels, T. Hsieh and J. P. Gilman, J. Chem. Phys., in press.

FIGURE LEGENDS

Figure 1. Breakdown Graph of the four butene isomers determined by TPE-CPI-MS corrected for the transmission function.

Figure 2. Breakdown graphs of cyclobutane and methylcyclobutane.

Figure 3. Ranges for stopping low energy electrons determined from ion arrival time distributions; range within which 97% of total ionization is produced. Comparison data for air and plastics are those of A. Cole, Radiation Res. 38, 7 (1969).

BREAKDOWN GRAPH OF BUTENES

Figure 1

BREAKDOWN GRAPH OF METHYLCYCLOPROPANE

Figure 2a

BREAKDOWN GRAPH OF CYCLOBUTANE

Figure 2b

Figure 3

PUBLICATIONS ARISING FROM THIS RESEARCH

A. Papers published or in press in refereed journals

1. A. J. Illies and G. G. Meisels, "High Pressure Chemical Ionization Source with Coaxial Electron Entrance and Ion Extraction Apertures", Anal. Chem. 52, 325 (1980); (reprints attached).
2. G. G. Meisels, T. Hsieh and M. J. Weiss, "Fragmentation of SO_2^+ Prepared in Selected Internal Energy States", Advances in Mass Spectrometry, Volume 8, 104 (1980); (reprints not yet available; copies of preprints were provided last year).
3. G. G. Meisels, G. M. L. Verboom and T. Hsieh, "Angular Momentum in Ion Molecule Reactions", Advances in Mass Spectrometry, Vol. 8, 32 (1980); (reprints not yet available; copies of preprints were provided last year).
4. G. G. Meisels, T. Hsieh and J. P. Gilman, "Ion Fragmentation from Non-Interconverting Electronic States", J. Chem. Phys. 73, 0000 (October 1980); (reprints not yet available; copies of manuscript attached).
5. G. G. Meisels, "Angular Momentum, The Principle of Equal A-Priori Probabilities, and the 'Intermolecular Entropy Correction' in Equilibria of Ions and Molecules in the Gas Phase", J. Amer. Chem. Soc. 102, 0000 (September 1980); (reprints not yet available; preprints provided last year).
6. C. W. Polley, Jr., A. J. Illies and G. G. Meisels, "Ion Mobilities under Chemical Ionization Conditions", Anal. Chem. 52, 0000 (October 1980); (reprints not yet available; preprints were provided last year).

B. Papers published in meeting proceedings

1. J. P. Gilman, T. Hsieh and G. G. Meisels, "Elimination of the Central Carbon in the Fragmentation of Propane Ion", 28th Annual Conf. on Mass Spectrom. and Allied Topics, New York, NY, May 1980.
2. T. Hsieh, J. P. Gilman, M. J. Weiss and G. G. Meisels, "Interconversion of Ion Structures: Nitromethane and Methylnitrite Ions", *ibid.*
3. G. G. Meisels, "Is the Intermolecular Entropy Correction in Gas Phase Ionic Equilibria Correct?", *ibid.*
4. T. Hsieh, J. P. Gilman, M. J. Weiss and G. G. Meisels, "Transmission Characteristics of Collimated Hole Threshold Photoelectron Detectors", *ibid.*

C. Papers submitted for publication

1. T. Hsieh, J. P. Gilman, M. J. Weiss, G. G. Meisels and P. M. Hierl, "Transmission Characteristics of Collimated Hole Threshold Photoelectron Detectors", *Int. J. Mass Spectrom. and Ion Physics*; accepted for publication; preprints attached.
2. R. Infante and G. G. Meisels, "Pyrolysis/High Resolution Mass Spectrometry of Green River Shale Kerogen", *Geochim. Cosmochim. Acta*, submitted for publication; manuscript attached.

ORAL PRESENTATIONS ARISING FROM THIS RESEARCH

- 1 - 3. 28th Annual Meeting on Mass Spectrometry and Allied Topics;
see items under Publications, section B.
4. American Chemical Society, National Meeting, Houston, TX, March 1980.
5. Gordon Conference on Radiation Chemistry, June 1980 (contributed short presentation): "Fragmentation of Methylnitrite Ions from Isolated Electronic States".
6. Gordon Conference on Radiation Chemistry, June 1980 (short contribution) "Range of 100 to 500 eV electrons".
7. Seminars on "Ion Molecule Reactions" at The University of Kansas, The University of Arkansas, and The University of Missouri.

OTHER CONTRACT RELATED ACTIVITIES

1. Chairman, Gordon Conference on Radiation Chemistry, June 1980.
2. Editor, Special Issue of Radiation Chemistry and Physics on "Mass Spectrometry and Radiation Chemistry"; to be published in 1981.