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

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Abstract

The methods for assessing track temperature in gases were examined and that based on differences in activation energies of abstraction reactions was developed using two techniques. The first is based on total product analysis of species which have iso- or n-propyl radicals as precursors. The other is concerned with the same radicals but employs $C_2^{14}H_4$ as a scavenger and the radical-sampling technique for quantitation of the two intermediates. In the gamma radiolysis of propane, the relative yields of the two radicals are independent of pressure between 0.005 and 0.02 g/cm³.

The analysis of lifetimes of ion-molecule reaction intermediates using a simple combination of RRKM and Langevin theory with retention of angular momentum in the complex was continued. It suggests that the third order rate constant derived from collisional deactivation experiments of CO_3^- should depend approximately on the $T^{-1.5}$ suggesting caution in the use of temperature dependencies to derive information on transition states.

Methodology of rate constant determinations by time resolved measurements was analyzed, and a new approach based on predicted arrival time distributions was developed. The rate constant for the dimer ion $(CO_2)_2^+$ with methane to give the displacement product $CO_2CH_4^+$ was evaluated as 1.6×10^{-9} cc/sec⁻¹.

CHEMICAL EFFECTS OF FISSION RECOILS

A temperature controlled fission radiolysis system has been designed, constructed and tested. While primary irradiation capsules are essentially identical to those employed previously, secondary containment and temperature control are new. (Figure 1). Temperature is maintained by a circulating butyl phthalate bath with appropriate safety features dictated by hazards analysis. Utilization awaits completion of the derrick required to move the assembly into the pool and adjust its position relative to the core. Consequently, we have no experimental data to report for fission initiated radiolysis.

Co^{60} GAMMA RADIOLYSIS OF GASES

Gamma radiolyses are performed primarily as a back-up to fission recoil radiolyses in order to assess possible complications arising from density effects alone. Our current objective is to assess track temperature using competitive reactions with known activation energies. In particular, we are concerned with the use of the hydrogen atom abstractions from propane to produce n-propyl and i-propyl radicals; bond strength of the secondary and primary radical differ by about 3.6 kcal/mole in this system.¹ Consequently, the relative yield of the two species should be temperature dependent. When radical concentrations are relatively high and combination is much faster than metathetical reaction with propane, as will normally be the case in the track, the abstraction reaction determines the relative yield. When radical concentrations are very low, such as in low pressure, low intensity gamma radiolysis, the equilibrium between the two species may be approached; in both cases, relative formation of n-propyl radicals should increase with temperature.

The relative yields of the two radicals can be estimated by three techniques. The first relies on total analysis for C_6 hydrocarbons. Together with known combination-disproportionation rate constants² for these encounters, one may calculate the relative yields of the two radicals from simple analysis based on the yields of 2,3-di-methyl-butane, 2-methyl-pentane, and n-hexane. Using a 10,000 Cie shipboard irradiator, with all samples initially at 20°C, propane was irradiated with and without small amounts of oxygen in the density range 0.005 to 0.020 g/cm³. Over this range, the relative yield of iso- and n-propyl radicals remains constant within $\pm 10\%$. The large disproportionation-combination ratios and their possible temperature dependence introduce some uncertainty.

This ratio and its sensitivity to temperature are reduced in the well-known radical sampling technique.³ This approach is based on the addition of a small amount of radioactive scavenger, ethylene, which adds hydrogen atoms produced by radiolysis of the bulk gas (methane, ethane or propane). Only a relatively small portion of the hydrogen atoms are so converted. The resulting radicals combine with the radicals derived from the bulk radiolysis, and monitoring radioactive content of products by Radio-gas chromatography permits quantitative assessment of the nature and yield of radicals. Scavengers other than ethylene may be employed, such as those which yield radicals by electron capture, but most of these liquify at somewhat too low a pressure, or contain elements with very high neutron absorption cross section to produce radioactive products, to be useful here.

Our existing gas chromatograph was modified by the addition of a proportional gas counter and the necessary power supplies and counters, and taken into use in mid-summer. Preliminary testing and calibration of the equipment have been completed, but no actual runs have been performed as yet.

A third approach may be based on specifically deuterium labeled propane, such as radiolysis of $\text{CH}_3\text{CD}_2\text{CH}_3$, followed by isotopic analysis of neutral products resulting from radical abstraction from propane, i.e. CH_3D or CH_4 from methyl radicals. The possibility of contributions by hydride transfer can be separated by assessing the yield of products arising from radical processes only through the addition of radical scavengers. Because this approach requires rather large amounts of expensive specifically labeled chemicals, it was not pursued.

MASS SPECTROMETRIC STUDIES OF RADIATION - INDUCED INTERMEDIATES

A. High pressure mass spectrometry.

The lifetime of intermediate complexes in ion-molecule reactions formed by collisions on a singular energy surface has been investigated further; the model involves the folding of an RRKM rate constant for specific collision energies and impact parameters into distributions of these quantities, on the assumption that angular momentum resulting from the collision encounter is preserved and lowers the barrier towards redissociation.

Conversion of the first order rate constant so obtained to a third order rate constant, assuming that the competitive collisional deactivation occurs with collision efficiency as determined by Langevin capture, leads to the suggestion that the third order rate constant varies as $T^{-1.5}$. In this model, the conversion of rotation to torsion is not a realistic interpretation, suggesting caution in the use of temperature dependencies to derive information on the transition state.⁴

Investigations into the rate of reaction of positive ions in carbon dioxide were initiated. At pressures in excess of a few tenths of one torr, the dimer ion $C_2O_4^+$ dominates as long as the system is scrupulously clean. The addition of even a small concentration of other species such as water or methane leads to a displacement reaction such as

and such product species are thought to be important in radiation induced corrosion in gas cooled reactors. Over the range of 4 to 8 V/cm/torr and at 423°C, the rate constant for this reaction was found to be $k_1 = 1.63 (\pm 0.13) \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. This is essentially equal to the ion-induced dipole rate constant for this process, $k_1(\text{theoretical}) = 1.61 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$.

The lifetime of intermediate complexes is normally determined experimentally by studying the competitive deactivation of the energetic complex with a neutral species. Methods for the direct determination of the deactivation efficiency using time resolved measurements were investigated. Since the extent of reaction in pure gases can only be altered by changing total pressure, the arrival time distribution method used in our laboratories is not directly applicable. The ion current ratio method, using the reactant and product ion currents, appears to advise itself but is based on the assumption that the reactive identity change does not affect residence time. This is a poor assumption when dimerization is involved since the heavier ion must drift more slowly. An approach was developed which relies on the independence of drift properties on the ratio of time to pressure which results from the invariable occurrence of the product of diffusion constant and time in diffusion equations. Over a limited range of pressures, arrival time distributions are therefore predictable when they are known at one pressure. This approach was investigated employing an unreactive ion, t-butyl ion in iso-butane, and found to be applicable over a pressure change of approximately 20%. The major complication is thought to arise from space charge effects and from the change in electron beam penetration into the ion chamber; the latter effect can be reduced by variation in electron gun potential and by moving the electron beam entrance to the rear of the chamber.⁵

Another approach to the study of the equilibrium position in dimerization reactions is an investigation of the reduced mobilities of the species involved. For the reaction

or analogues such as reaction 1, reduced mobilities of O^- and CO_3^- should be identical if the equilibrium reactions proceed repeatedly in both reactions during the residence time of the charge in the source. At very low pressures,

when reaction 2 does not proceed significantly in the forward direction, the mobility of O^- should be larger, while at very high pressures where the reverse reaction is essentially inhibited by collisional deactivation, CO_3^- should have a lower mobility. Data were obtained for this system which show that at 0.21 torr the drift velocities of O^- and CO_3^- differ as expected and begin to approach each other as the residence time is increased by decreasing the applied field. Signal intensity of O^- decreased so much that identical arrival times were not achieved. Experiments at other pressures were undertaken, but the phenomenon can only be observed over a rather narrow range of pressures and field strengths. Experimental uncertainty, resulting largely from inadequate temperature control, forbade the acquisition of data with sufficient accuracy to allow reliable conclusions. Further work awaits the construction of a modified ion source.

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FIGURE 1

Secondary Containment Vessel

- A. Vent Valve
- B. Electrical Connector
- C. Safety Line Ring
- D. Support Coupling
- E. Pressure Transducer
- F. Motor
- G. Secondary Reservoir
- H. Drive Coupling
- J. Primary Cell
- K. Retaining Clasp
- L. Bath Vessel
- M. Rotating Support

Secondary Vessel

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PUBLICATIONS ARISING FROM THIS CONTRACT

Photoionization Processes at Threshold: Direct and Autoionization and Franck-Condon Factors for Simple Molecules. C.F. Batten, J.F. Taylor, and G.G. Meisels, J. Photochem. 5, 1965 (1976), abstract.

Lifetimes of Intermediate Complexes in Ion-Molecule Reactions, G.G. Meisels, F. Botz and E.F. Heckel, Proc. 24th Annual Conf. Mass Spectrometry and Allied Topics, San Diego, CA (1976).

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ORAL PRESENTATIONS ARISING FROM THIS GRANT

"The Study of Ion-Molecule Reaction Antics and Equilibria in High Pressure Sources"; Series of four lectures, University of Warwick, England, July 1976.

"Lifetimes of Intermediate Complexes in Ion-Molecule Reactions", paper presented at the 7th International Conference on Mass Spectrometry, Florence, Italy, September 1976; also, 24th International Meeting on Mass Spectrometry and Allied Topics, San Diego, CA, May 1976.

"Evaluation of Rate Constants in High Pressure Mass Spectrometry by Time Resolved Measurements", Symposium on Chemical Applications of High Performance Mass Spectrometry, Lincoln, NE November 1976.