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ABSTRACT

The chemical properties of atomic phosphorus, hydrogen and mercury have been investigated with emphasis on the properties of translationally or electronically energetic atoms. Excitation processes have included neutron activation, ultraviolet irradiation, thermal dissociation, electron bombardment, electrical discharge and field ionization. The quenching of $\text{Hg}(6^3\text{P}_1)$ and $\text{Hg}(6^3\text{P}_0)$ atoms by hydrogen and hydrocarbons in the gas phase and by hydrocarbons in the solid phase have been studied. Gas-solid reactions of energetic tritium species with thin films of hydrocarbons have been investigated. Evidences of both hot and thermal reactions were observed in varying proportions depending upon the means by which the energetic tritium species were produced.

Mercury Spectra and Photosensitized Reactions in Low Temperature Matrices

Abstract of the Ph.D. Thesis of Timothy Jones, Kansas State University, 1976.

The absorption spectra of Hg trapped in low temperature matrices of poor, moderate and efficient quenchers of excited Hg have been recorded. Host molecules included Ar, Kr, Xe, N₂, CO, C₁ to C₆ alkanes (including the C₄ and C₅ branched chains), straight chain C₂ to C₆ alkenes, and acetone. The spectra consist of essentially two or three multiplet structures. Doublet or triplet bands appeared in the vicinity of the Hg $6(^3P_1 \leftarrow ^1S_0)$ transition at 2536.5 Å, in all of the matrix spectra (N bands). Very weak bands appeared about 200 Å to the blue of this line in some of the matrix spectra. Stronger satellite bands appeared from 2250 to 2100 Å in all of the matrix spectra. The latter two bands are designated S bands.

The longer wavelength component of the N bands was attributed to the host-perturbed Hg $6(^3P_1 \leftarrow ^1S_0)$ transition. Perturbation of this transition by long range interactions between non-nearest-neighbor Hg atoms are thought to be responsible for the other components of the doublet or triplet N bands.

Transitions between dimeric or polymeric Hg atoms appear to be responsible for both the weaker and stronger S bands.

All of the absorption bands shifted to longer wavelengths with increasing host molecular weight and size. The Hg/CO absorption was out of line. The N band of the Hg/CO spectrum occurred farther to the red than in any of the Hg/alkane spectra. The weaker S bands were observed only in the spectra of matrices containing the smaller host molecules.

Hg/alkene N bands were characteristically broader and had lower maximum optical densities than corresponding Hg/alkane N bands. The relative integrated absorption intensities of the Hg/alkene and Hg/alkane N bands were,

for the most part, about equal.

N bands in the Hg/alkane spectra were drastically reduced and both the N and S bands of the Hg/acetone spectrum were reduced significantly by short periods of strong 2536.5 Å irradiation. The spectra of Hg/C₂H₄ and Hg/C₃H₆ matrices were unaffected by UV irradiation. Prolonged irradiation caused some rearrangement of the Hg/larger-alkene matrix spectra.

Bleaching of the Hg/alkane and Hg/acetone matrix spectra have been taken as indirect evidence of stabilized transients formed during photolysis. Attempts to directly observe such transients by UV and IR spectroscopy were unsuccessful.

The lack of spectral change in the Hg/alkene matrices is probably evidence against the formation of stabilized (Hg-alkene) complexes.

The products from solid phase Hg photosensitized reactions were the same as those observed from gas phase Hg photosensitization. The solid phase quantum yields were about three orders of magnitude lower than those in the gas phase.

Three spectral features were used in an attempt to establish correlations between gas phase quenching efficiencies (k_Q) and the trapped Hg spectra. These were 1) shift ($\Delta\bar{\nu}$) of the longer wavelength component of the N band from the 2536.5 Å transition, 2) halfwidth ($\bar{\nu}_{1/2}$) of the N bands, and 3) the N band integrated absorption intensities ($\int A d\bar{\nu}$).

k_Q and $\Delta\nu$ appeared to be linearly related through a series of similar molecules. For example, two different straight line plots of $\Delta\bar{\nu}$ vs k_Q were obtained in the alkanes (propane through n-hexane) and in the alkenes (ethylene through 1-hexene).

The N band halfwidths appeared to be dependent upon the extent of interaction between the Hg and host molecules as well as upon the relative Hg-host orientations.

Although the integrated absorption intensities for equal amounts of Hg varied widely among the matrix spectra, there was no simple relationship between $\int A d\tilde{\nu}$ and properties of the host (eg. polarizability, k_Q , etc.). A comparison of the spectra of Hg trapped in low temperature noble gas and alkane matrices did indicate some intensity enhancement by the alkane hosts.

The Reactions of 10 KeV T^+ and T_2^+ with Propene at 77°K

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Field ionization has been used as a means of generating hydrogen ions for the study of their reactions with propene films. This technique of producing hydrogen ions was selected for several reasons: (a) a reaction arrangement could be constructed that could be operated as a closed system and thus would require the use of only small amounts of tritium as a tracer for hydrogen, (b) the problem of atomization of hydrogen associated with ionization sources using thermionic electron emitters is eliminated, and (c) while not studied as yet, the chemical properties of a wide range of ion energies could be investigated.

Experimental

The reaction vessel was constructed of Pyrex glass. A thin film (1.5×10^{-6} mole) of propene was condensed at 77°K on a 6 cm^2 glass target that was coated with a layer of silver to provide a conducting surface. Tritium gas at a pressure of 0.4 to 1.0 millitorr was ionized at a tungsten tip which was positioned at a distance of 2 or 5 cm from the target. The tungsten tip was prepared by chemically etching the end of a 10 mil tungsten wire with molten sodium nitrite. The tungsten tip was connected to the positive pole of a high voltage power supply which had a variable output. The target was maintained at near ground potential. The current of positive ions was measured with an electrometer which was connected through a safety resistor to the target. Reactions were carried out for periods of 3-6 minutes at tritium ion currents in the range of 10^{-10} to 10^{-9} ampere.

Potentials of approximately 10,000 volts were required to produce this current. Once established, the current remained constant throughout the reaction, and no detectable change in tritium pressure was observed in the closed system during the course of the reaction.

Both atomic and molecular ions were produced at the tungsten anode.¹ No attempt was made at this stage to measure the relative amounts of the two ionic forms.

The reaction products were separated gas chromatographically using a 10 ft. column of 40% AgNO₃ in ethylene glycol on chromosorb P in series with a 15 ft. column of 15% isoquinoline on chromosorb P. The amount of tritium in each product was measured in a flow-through ionization chamber connected to a vibrating reed electrometer.

Results

Listed in Table I is the average product distribution of tritium labeled products, condensable at 77°K, that resulted from the bombardment of propene films with 10 KeV tritium and tritium molecule ions.

Table I. Distribution of Products* from the Reactions of 10 KeV Tritium Ions with Propene at 77°K

Reaction Product	Relative yield
C ₂ H ₄ (C=C)	92
C ₃ H ₆ (C-C=C)	100
C ₃ H ₈ (C-C-C)	35
C ₄ and above	50

* Condensable at 77°K. Average of seven reactions.

Discussion

The principal reactions that occurred on bombardment of propene films with 10 KeV tritium and tritium molecule ions were substitution of T for H

and substitution of T for CH_3 . The product distribution would indicate that the chemical properties of these species are similar to those of nuclear recoil tritium species which in the gas phase also reacted principally by substitution of T for H and T for CH_3 .² In contrast to these substitution reactions, tritium species from thermal atomization,³ electron impact on T_2 ,⁴ and low pressure gaseous discharge⁵ all, in varying degrees, underwent more addition than substitution reactions with propene.

These limited results indicate that field ionization could be a useful technique to apply in the study of the reactions of energetic tritium and other species with solids.

References

1. M. G. Inghram and R. Gomer, J. Chem. Phys., 22, 1279 (1954).
2. J. K. Lee, B. Musgrave and F. S. Rowland, J. Amer. Chem. Soc., 82, 3545 (1960).
3. D. W. Rathburn, K. Knarr and H. C. Moser, Trans. Faraday Soc., 67, 2333 (1970).
4. R. D. Shores and H. C. Moser, J. Phys. Chem., 72, 1 (1968).
5. K. Finney, M. S. Thesis, Kansas State University, 1970.

Summary of publications under Contract EY-76-S-02-0584.*000
FORMERLY: E(11-1)-0584

D. W. Setser, H. C. Moser, and R. E. Hein, "Neutron and Gamma Irradiation of Phosphorus Trichloride," J. Am. Chem. Soc., 81, 4162 (1959).

S. H. Shipotofsky and H. C. Moser, "Gas Chromatographic Analysis of Some Volatile Phosphorus Compounds," Anal. Chem., 33, 521 (1961).

R. D. Shores, and H. C. Moser, "Reactions of Tritium Atoms with Frozen Hydrocarbons," J. Phys. Chem., 65, 570 (1961).

T. J. Clark and H. C. Moser, "Reactor-Irradiated Phosphoryl Chloride," J. Inorg. Nucl. Chem., 17, 210 (1961).

L. F. Grantham and H. C. Moser, "Radiation Induced Exchange of Phosphorus in the PCl_3 - POCl_3 System," J. Phys. Chem., 66, 863 (1962).

H. C. Moser and R. D. Shores, "Reactions of Tritium Atoms with Frozen Cyclopropane," J. Phys. Chem., 66, 2272 (1962).

A. A. Sandoval, H. C. Moser and R. W. Kiser, "Ionization and Dissociation Processes in Phosphorus Trichloride and Diphosphorus Tetrachloride," J. Phys. Chem., 67, 124 (1963).

A. A. Sandoval and H. C. Moser, "Preparation of Diphosphorus Tetrachloride," Inorg. Chem., 2, 27 (1963).

H. B. Yun and H. C. Moser, "Reactions of Energetic Hydrogen Atoms with Solid Films of Propene at 77°K," J. Phys. Chem., 67, 2806 (1963).

H. C. Moser, Philip Nordin and J. K. Senne, "Labeling Carbohydrates by Exposure to Energetic Tritium Atoms," Intern. J. Appl. Rad. Isotopes, 15, 557 (1964).

K. W. Watkins and H. C. Moser, "Reaction of Tritium Atoms with Films of Solid Ethylene. Disproportionation and Combination of Ethyl Radicals at 63°K," J. Phys. Chem., 69, 1040 (1965).

H. B. Yun and H. C. Moser, "Disproportionation and Combination of Tritium-Labeled Isopropyl Radicals," J. Phys. Chem., 69, 1059 (1965).

P. Nordin, H. C. Moser and J. K. Senne, "Tritiated Starch Granules," Biochem J., 96, 336 (1965).

K. W. Watkins and H. C. Moser, "Reactions of Tritium Atoms with Tritium Labeled Isopropyl Radicals at 63°K," J. Phys. Chem., 70, 1137 (1966).

P. S. Gill, R. E. Toomey and H. C. Moser, "Reactions of H and T Atoms with Carbon at 77°K," Carbon, 5, 43 (1967).

M. W. Haseltine and H. C. Moser, "Oxidation of Radon in Aqueous Solution," J. Amer. Chem. Soc., 89, 2497 (1967).

R. D. Shores and H. C. Moser, "Reactions of T Atoms Produced by Electron Impact on T₂ with Solid Propene and Propane," J. Phys. Chem., 72, 1 (1968).

P. Nordin, H. Moser, G. Rao, N. Giri and T. Liang, "Labeling of Starch Granules by Bombardment with Tritium Atoms", Die Starke, 22, 256 (1970).

A. C. Vikis and H. C. Moser, "Quenching of Hg(6^3P_0) Atoms by Hydrogen and Hydrocarbons," J. Chem. Phys., 53, 1491 (1970).

A. C. Vikis and H. C. Moser, "Investigation of the Quenching of Excited Mercury Atoms by the Alkanes," J. Chem. Phys., 53, 2333 (1970).

C. D. Finney and H. C. Moser, "Low-Energy Electron Radiolysis of Methane," J. Phys. Chem., 75, 2405 (1971).

D. W. Rathburn, K. Knarr and H. C. Moser, "Pressure Effects in Hydrogen Atom Reactions with Frozen Propene", Trans. Faraday Soc., 67, 2333 (1971).

T. C. Liang, P. Nordin and H. C. Moser, "Distribution of Tritium in d-Glucose and Starch Labeled by Tritium Atom Bombardment," Carbohydrate Research, 27, 473 (1973).