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MASTER

COMPUTER SIMULATION OF HOT - ZONE REACTIONS (II)

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INTRODUCTION

The next step in the computer simulation of hot-zone reactions involved a modification on the model previously introduced (2). Using

(2) Vincent C. Anselmo, T. King, and T. Rekart,
 AEC Report COO-1618-7.

the same assumptions, i. e., considering that the recoiling atom dis-locates many atoms in its path toward thermalization, and that random recombination is responsible for fragmented chemical species that then may react with the solvent to produce the chemical activities we eventually see. The original paper assumed ^{32}P as the recoiling species. Analysis of the results indicated that the nature of the recoiling species needed modification. In this work, HP and HPH, for recoil ^{32}P produced in $\text{NH}_4\text{H}_2\text{PO}_2$, were considered the recoiling species. The following ratio of atoms and species was used: HP:HPH:N:H:O::59:59:118:528:236 (the ratio of atoms was adjusted slightly to make the number of atoms fit the matrix), and then these were distributed randomly in a 10X10X10 matrix. The atoms and species were moved randomly within the matrix in a step-wise manner. After each step or pass the computer was asked to print out the new matrix. The procedure was repeated 10 times because at that time the number of each species had essentially reached equilibrium. In addition, it was assumed that nitrogen, oxygen and hydrogen could achieve a maximum valency of two while phosphorus could be tetravalent. This was to provide more reality to the model and to reduce the complexity of the resulting species. The reliability of the model was tested by comparing the

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results from the computer simulation with experiment results from thermal-neutron irradiated ammonium hypophosphite dissolved in aqueous solvent and liquid ammonia. (3).

(3) Vincent C. Anselmo and Ernest Sanchez, Radio chim. Acta in Press; AEC Report COO-1618-10.

DISCUSSION

In presenting and discussing the results, we made some very broad and general assumptions because some very unusual species occurred. In Table I we list most of the fragments produced in the simulation, followed in columns 2 and 3 by their expected product on solution in water and liquid ammonia, respectively. In Table II are found the fractions as the several chemical species. The arrows indicate whether the species increases, decreases, or remains essentially constant during the 10 computer passes or as a result of isothermal annealing in the compared experimental result. While there are some points of similarity between the simulation and the experimental, there are more serious points of dissimilarity. Particularly disturbing are the discrepancies with the sample dissolved in liquid ammonia. The most responsible explanation is that the nitrogen containing fragments produced in the solid are difficult to trace in aqueous solution after reaction with liquid ammonia. Even assigning the 9% as simple reduced phosphates is a gross extrapolation based upon assumptions from the little known chemistry of phosphoramidates.

In conclusion, this particular simulation does give some points of similarity with experiment, especially for aqueous solvent, but leaves much to be desired in terms of quantitative detail, and even qualitative detail for the liquid ammonia reactions.

(1) This work performed at New Mexico Highlands University, Las Vegas, New Mexico, 87701, under contract AT(11-1)-1618, with the United States Atomic Energy Commission.

TABLE I

Major Fragments Produced in the Simulation and Their Possible Reaction Products on Solution in Aqueous Solvent and Liquid Ammonia.

Fragment	Solution in Aqueous Solvent	Solution in Liquid NH_3 Followed by Solution in Aqueous Solvent.
HPO	p^3	phosphoramidates
HP_xO $x = 2, 3$	complex reduced phosphates	$\text{p}^1, \text{p}^3 (?)$
HPO_x $x = 2, 3$	p^3	p^1, p^3
HPN	phosphoramidates	phosphoramidates
HP HPH	p^1, p^3	phosphoramidates
HPN O HPN	phosphoramidates	phosphoramidates
HPPN PN_x $x = 1, 2, 3, 4$	complex phosphoramidates	complex phosphoramidates
HP_xO $x = 2, 3$	complex reduced phosphates	phosphoramidates
PH_3 PH_4 H_2PO	p^1, p^3	phosphoramidates
HPN_2 NOPN_4	phosphoramidates	phosphoramidates
$\text{HP}_x\text{-PN}$ $x = 1, 2$	complex phosphoramidates	complex phosphoramidates

TABLE II

Comparison Between Simulation Predictions and Experimental Results as Percent Particular Species.

Species	Fragments with Aqueous Solvent	Experimental ^(a)	Fragments with Liquid Ammonia	Experimental
	Simulation		Simulation	
Simple Reduced Phosphates ^(b)	45 ↓	47 ↑	9 ↑	56 ↑
Complex Reduced Phosphates ^(c)	15 ↑	23 →	0	20 ↑
Simple Phosphoramidates ^(d)	37 ↑	22 ↑	69 ↓	21 ↓
Complex Phosphoramidates ^(e)	5 ↑		22 ↑	4 →
Orthophosphate	0	3 →	0	0
Complex Orthophosphate ^(f)	0	6 ↓	0	7 →

(a) From ref. (2): Samples annealed at $67 \pm 2^\circ\text{C}$ for at least 5 hours.

(b) P^1 and P^3

(c) Any phosphorus containing species of more than one phosphorus atom

(d) For example phosphoramidate, phosphordiamidate, or phosphoramidite.

(e) Any phosphorous-nitrogen containing species of more than one phosphorus atom.

(f) High molecular weight phosphate.