4-13
COMPUTER SIMULATION OF HOT-ZONE REACTIONS

Vincent C. Anselmo, Theodore King (1) and Theodore Rekart
Department of Chemistry
New Mexico Highlands University
Las Vegas, New Mexico 87701

600-1618-7
MASTER

(1) Assistant Director, Computer Center, New Mexico Highlands University.

INTRODUCTION

The hot-zone model (2), that was proposed as a rationalization for the chem-

(2) Harbottle, G., and N. Sutin, Advances in Inorganic Chemistry and Radiochemistry, 1, 268 (1959).

ical effects following a nuclear transformation in the solid state, is based on the assumption that a recoiling atom generates a large number of dislocated atoms or fragments in reaching thermal equilibrium following recoil from its original chemical environment. The energy for this recoil is provided by the nuclear event, e.g., radiative-neutron capture, beta decay, isomeric transition, etc. A computer simulated model is being developed that will provide not only a rationalization for the final chemical products observed for a particular chemical system, but also should be useful in explaining isothermal-annealing and solvent effects. If it is assumed that changes on annealing are the result of recombination of fragments within the hot-zone, then this model should be able to relate to the final products and the rate at which they are formed. The chemical system that is of particular interest here is neutron-irradiated ammonium hypophosphite. The selection of this system is based on experimental evidence that has already been reported (3), i.e., the appearance of at least two unique activities, viz.,

(3) Anselmo, V. C., and E. Sanchez, Radiochim. Acta, in press.

species containing ^{32}P that are not simple oxygen containing oxy-anions, but rather belong to the series of amidophosphates.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

REPRODUCTION OF THIS DOCUMENT IS UNLIMITED.

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.

In addition, solution of neutron-irradiated ammonium hypophosphite in liquid ammonia prior to its analytical separation, results in three additional activities which have been assigned to other nitrogen containing oxy-anions. These experiments seem to indicate that within the solid there is some reaction between a phosphorus fragment and a nitrogen fragment which produces, in the case of aqueous solution, a nitrogen-containing phosphorus oxy-anion. On solution in liquid ammonia, a fragment that might otherwise produce a simple phosphorus oxy-anion now produces one containing nitrogen.

If the model is successful, it will then provide information not only on the distribution of phosphorus oxy-anions, but it should be able to show how interruption of the annealing by solution, in either aqueous solvent or liquid ammonia, can change the distribution of activities.

The model was conceived as follows. In the first approach, 1000 atoms were taken as constituting the hot-zone. The ratio of atoms was taken to be the same as the ratio of atoms in the original salt. For the case of ammonium hypophosphite, this was taken to be $N:P:H:O::1:1:6:2$. These were then randomly distributed in a $10 \times 10 \times 10$ matrix using a random number generator in the computer. This provides a cubic array of atoms and each atom is given the following random choices: first, the atom can either move or not move. If it does move it moves a unit distance in the x direction. Second, it again is given the choice of not moving or moving a unit distance in the y direction. Finally, it is given the choice of not moving or moving a unit distance in the z direction. Effectively, this means that the atom, which can be pictured as lying in the center of a solid exhibiting the sodium chloride type lattice, can move to any one of the 26 positions represented by its six nearest neighbors, the 12 next nearest neighbors, or the eight neighbors next farthest removed. This operation is performed for each atom under the boundary condition that no atom can leave the array. At the end of the operation the computer prints out the new array as well as the number of all species present.

The new atomic combinations are analyzed and a decision is made as to their behavior on solution in aqueous solvent and liquid ammonia. [The stable species, e.g., N_2 , H_2 and O_2 are removed by considering their lattice sites to be vacant. The operation is then repeated with the new distribution. This sequence of removal of stable species and repetition is continued until there are no reactive species remaining, or until the distribution of these species is unchanged.] In addition, a decision is made concerning the stability of some unusual species that are formed. In particular, bond energies are invoked in the decision, leaving the most stable bi- or tri-atomic entity, and removing the other(s) to the nearest vacancy.

DISCUSSION

The results of one pass, using the procedure described above, are shown in Tables I, II and III. In Table I are shown all the combinations formed in this first pass while Table II lists the phosphorus-containing fragments, their number, and products on solution in aqueous solution, as well as their possible products on solution in liquid ammonia. The last column reflects a speculation on what the products formed on initial solution in liquid ammonia might become on further solution in aqueous solvent. In Table III there is a comparison of the distribution of the stable entities against the experimental evidence. The results illustrate why the model is being altered with respect to the primary fragment. The predicted high abundance of orthophosphate is not compatible with the results. Experimentally, the fraction as orthophosphate is very small in irradiated hypophosphites. If this model is followed to its logical conclusion, only orthophosphate should be observed if the irradiated material could be dissolved without any fragment recombination occurring.

In conclusion this model represents a first attempt at simulation of reactions in the hot-zone. It recognizes the importance of the solution process on the distribution of activities. Further work on the model will change the identification of the initial fragments and should provide more information on the ammonium hypophosphite system. The model is limited because it only considers reaction

in the hot-zone. Other areas of reactivity are possible since a study of the spectrum of gamma-rays from a nascent ^{32}P atom shows that not all of the events will lead to a high energy phosphorus atom. There is a finite probability that the phosphorus atom will either emit a low energy photon, or emit two simultaneously at angles that cancel the recoil effect. Also, there is still to be explained the presence of the high-molecular-weight fraction.

Table I

**DISTRIBUTION OF SPECIES FOLLOWING FIRST PASS IN COMPUTER
SIMULATED MODEL FOR REACTIONS IN THE HOT-ZONE**

Species	Number	Species	Number
OPH	1	NOH	2
N	36	NHO	1
H	223	HNH	2
HO	26	NN	4
HH	64	PP	3
HOH	8	OHO	3
OHH	6	NO	3
NHOH	1	ON	4
OH	24	HOH	1
P	40	HNHH	1
O	70	HPO	2
NH	17	NPH	1
HHH	12	OP	4
OO	6	HHHN	1
PHHO	1	NHPH	1
HPH	1	OOH	1
HN	10	PPO	2
PO	4	ONHH	1
NHH	5	PHHH	1
NP	1	NOH	1
HPHH	1	HNO	1
NP	12	PN	1
HHHHH	1	OHHP	1
HNO	9	HPN	1
PH	9	PPH	1
HHHH	2	PNO	1
OPO	1	POOP	1
HPN	1	OOP	1

Table II

REACTIONS OF PHOSPHORUS CONTAINING FRAGMENTS FORMED IN PHOSPHORUS CONTAINING FRAGMENTS
FIRST PASS WITH AQUEOUS SOLVENT AND LIQUID AMMONIA

Fragments (number)	Most Stable Result	Product With Aqueous Solvent	Product With Liquid Ammonia ^(a)	Final Product on Solution in Aqueous Solvent ^(b)
OHP (1)	HP + O	O	HP(NH ₂) ₃	P ³ -N/N-P ³ -N
OHHP (1)	HP + OP	O		
P (40)	-	OPO	P(NH ₂) ₄	P ⁵ -N/N-P ⁵ -N
HPH (3)	-	HPH	H ₂ P(NH ₂) ₂	P ¹ -N
OOP (1)	OP + O	OPO	OP(NH ₂) ₃	P ⁵ -N/N-P ⁵ -N
OP (8)	-	O		
HNP (1)	NP + H	NPO	P(NH ₂) ₄	P ⁵ -N/N-P ⁵ -N
NP (2)	-	O		
HP (23)	-	HPO	HP(NH ₂) ₃	P ³ -N/N-P ³ -N
OPO (1)	-	OPO	O ₂ P(NH ₂) ₂	N-P ⁵ -N
HPN (2)	-	HPN	HP(NH ₂) ₃	P ³ -N/N-P ³ -N

a) These are represented without charges because they are intermediary species and not directly observed.

b) Many of these products are speculative, since their precursors in liquid ammonia are not known and so the chemistry is obscure. An extension of the Blaser notation is used, where P³-N and N-P³-N are ortho-, mono- and diamidophosphite.

Table III

COMPARISON BETWEEN FIRST PASS RESULTS IN THE COMPUTER
SIMULATION AND EXPERIMENT (3) REPRESENTED AS % ^{32}P

Aqueous Solvent			Liquid Ammonia		
Species	Model	Experiment ^(a)	Species	Model	Experiment ^(a)
P^5	54	~ 0	$\text{P}^5\text{-N/N-P}^5\text{-N}$	58	37(c)
P^3	29	23	$\text{P}^3\text{-N/N-P}^3\text{-N}$	34	
$\text{P}^4\text{-N}$	5.4	17	$\text{N-P}^4\text{-P}^4\text{-N}$	5.4	
$\text{P}^5\text{-N}$	4.3	8	$\text{N-P}^4\text{-P}^3\text{-N}$	1.1	3(d)
P^1	3.2	17	$\text{N-P}^5\text{-O-P}^5\text{-N}$	1.1	
$\text{P}^3\text{-N}$	2.2	(b)	P^1	0	30
$\text{P}^4\text{-P}^3$	1.1	0	P^3	0	7
$\text{P}^5\text{-O-P}^5$	1.1	11	$\text{P}^4\text{-P}^4$	0	3
			$\text{P}^5\text{-O-P}^5$	0	8

(a) Results from experiments with no annealing other than that which occurred during the irradiation.

(b) This species has not been studied on an anion exchanger so it could be part of $\text{P}^5\text{-N}$ activity.

(c) This represents the percent of all nitrogen containing activities eluted faster than ^1P . They have been assigned to simple nitrogen containing phosphorus oxy-anions.

(d) Represents the percent ^{32}P as a condensed amidophosphate of unknown complexity.