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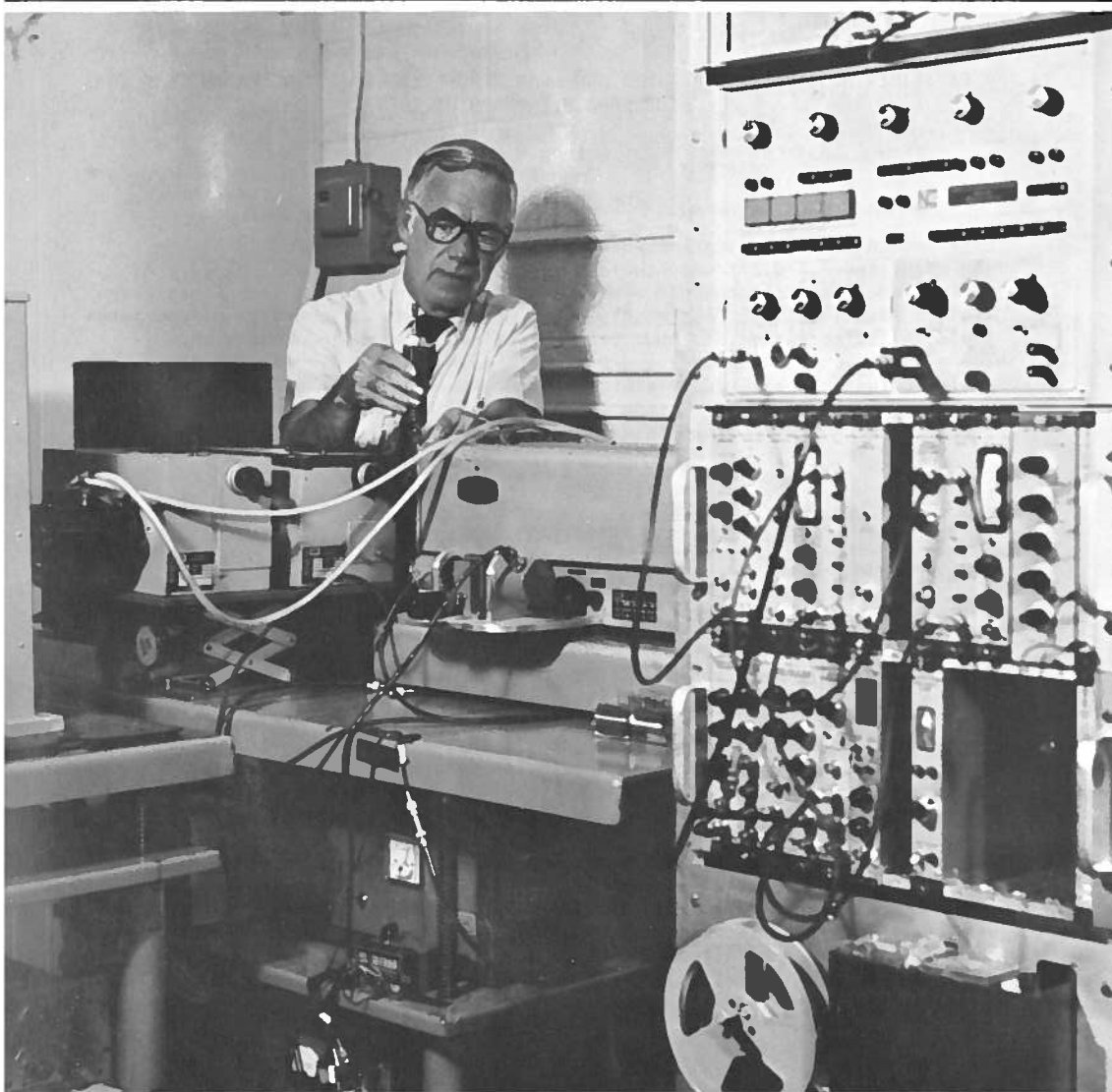
# CHESAPEAKE CHEMIST

MARYLAND SECTION  
AMERICAN CHEMICAL SOCIETY

VOL. XXXIV

MARCH, 1976

NUMBER 3



CHEMISTRY AT THE HEAD OF THE BAY

There has been chemical research related to ordnance at the Aberdeen Proving Ground since its beginning in 1918. When the Ballistic Research Laboratories were started at APG in 1938, a physical chemistry unit was an important part of the original organization. Some of the outstanding chemists who have been on its staff (some in uniform) since then include John Baldeschwieler, Tucker Carrington, F. P. Del Greco, Charles P. Fenimore, David Golden, J. H. Frazer, Fred Kaufman, George Kleinspehn, Lester P. Kuhn, Fred Morse, Joseph Morse, Karen Morse, J. W. Parry, and many others. And this list does not include any who are active staffers today!

The future may diminish the amount of chemistry done at the BRL, but not its quality. The Editors are pleased to dedicate this issue of THE CHESAPEAKE CHEMIST to the chemists on the Chesapeake who are part of the U. S. Army's BALLISTIC RESEARCH LABORATORIES.

*JSF*

EXPERIMENTAL TRIPLET LIFETIMES AND MEAN ZERO-FIELD SPLITTING PARAMETERS ( $D^*$ ) FOR SOME NITRONAPHTHALENES

Ingo W. May  
John R. Kelso  
Interior Ballistics Laboratory

Experimental triplet lifetimes have been obtained for 1-nitronaphthalene (48 msec) and 1,4-dinitronaphthalene (21 msec) in EPA solutions at 77 K by luminescence spectroscopy and electron spin resonance. Both techniques have yielded identical lifetimes within experimental error. In addition mean zero-field splitting parameters have been determined for 1-nitronaphthalene ( $D^* = 0.0893 \text{ cm}^{-1}$ ) and for 1,4-dinitronaphthalene ( $D^* = 0.0818$ ). These values indicate that the excited triplet state for these ( $\pi^*$ ,  $n$ ) states is no longer localized within the nitro group which implies that electronic charge is transferred from the nitro group into the aromatic ring.

\*\*\*\*

RAPID MULTIBASE PROPELLANT ANALYSIS TECHNIQUES

J. Omar Doali  
Interior Ballistics Laboratory

This task involves the application of high performance liquid chromatography as the primary instrument in the analysis of all organic components in conventional type classified United States propellants. Compounds to be separated and quantified include diphenylamine, 2-nitrodiphenylamine, 2,4-dinitrotoluene, ethyl centralite, diethylphthalate, dibutylphthalate, nitroglycerin, nitroguanidine, and nitrocellulose. Minimization of the required number of separation conditions is a prime objective.

Investigations will be carried out using both adsorption type substrates and partitioning substrates to determine which column packing materials are most applicable. Gradient elution will be employed in an attempt to achieve a "one shot" separation and determination of all organic components with the exception of nitrocellulose. Gel permeation chromatography will be investigated as a method of determining the nitrocellulose content of propellants.



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COVER: Mr. John R. Kelso of the BRL adjusts a digital spectrophotometer for the detection of luminescence in nitronaphthalenes. (See p. 2).

March Ed. -in-charge: E.F.

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Kevin J. White, Cornellus U. Morgan, and John R. Kelso  
Interior Ballistics Laboratory

The objective of this task is to determine the radical mechanisms involved in the ignition of propellants and propellant ingredients. Electron Spin Resonance spectroscopy is the technique used to detect these radical intermediates. Compounds such as nitrate esters and aldehydes were pyrolyzed and the reaction products were studied by either trapping out on a cooled substrate or by observing the gas phase radical products. Several techniques were employed for decomposing the compounds and trapping the products for study by electron spin resonance. A resistively heated capillary oven was used to decompose a flowing mixture of the nitrate ester or aldehyde. The products emerged into a vacuum system and were trapped out at 77K on a substrate located in the cavity of an ESR cavity. Temperatures of up to 1000K and residence times of 10 msec could be achieved in this way. In order to shorten this residence time a second oven was constructed which could be heated with a CO<sub>2</sub> laser. The reaction zone length could be shortened such that residence times of under 1 msec could be achieved. N-propyl nitrate yielded the CH<sub>3</sub>CHCH<sub>2</sub>ONO<sub>2</sub> radical and an unidentified resonance. Ethyl nitrate produced CH<sub>3</sub>CHONO<sub>2</sub> plus NO<sub>2</sub>. When acetaldehyde, propanal and isobutanal (diluted with helium) were pyrolyzed in the laser heated oven the same results were obtained as with the resistively heated oven. The predominant radicals for these three aldehydes were CH<sub>2</sub>CHO, CH<sub>3</sub>CHCHO and (CH<sub>3</sub>)<sub>2</sub>CHO.

In order to decrease the possibility of reactions taking place during the trapping process, a new dewar was installed, capable of achieving trapping substrate temperatures of 10K. Laser pyrolysis experiments were carried out on nitrocellulose, β-methyl glucoside tetranitrate and cellobiose octanitrate. Compounds were pyrolyzed under vacuum and products deposited in the cooled substrate and examined by ESR. NO<sub>2</sub> was the only paramagnetic species observed and was detected for all compounds.

Slow thermal decomposition experiments were also carried out with isolation of products in nitrogen and argon matrices at 10K. Compounds decomposed in this manner were nitrocellulose, 1,3,5,7-tetra nitro, 1,3,5,7-tetra azacyclooctane (HMX), TNT and the nitrated sugars. A very brief summary is given here of some of the results from this study:

1. The slow and fast decomposition of nitrate esters yield NO<sub>2</sub>.
2. A second radical species is also produced during the slow decomposition. The concentration of this species relative to NO<sub>2</sub> increases with decomposition temperature and with the addition of lead salicylate.
3. Since the primary alkoxy radical was not detected it is believed that secondary reactions take place in the condensed phase.
4. HMX yields the radical products detected in NC decomposition and an additional species. The relative concentration of this species is temperature dependent.

NOTE TO OUR READERS: Do you have any interesting chemistry you'd like to share with the Maryland Section? Send it to any member of the Editorial Staff of THE CHESAPEAKE CHEMIST. It will eventually appear. No refereeing, no charges, and only a minimum of editing (for space). Please avoid complicated mathematical formulas--they're hard to type! Industrial contributors must have suitable publication authority.

Douglas A. Ringers  
Applied Mathematics and Science Laboratory

The knowledge of the basic science of materials such as 1,3,5-trinitro-hexahydro-s-triazine (RDX) and its eight-membered ring analogue, HMX, is of the utmost relevance to their use as chemical explosives.

One of the tools we are using is the multiple scattering x-alpha method (MSXα), a self-consistent field method which has several features of the xa method which make it generally superior to any Hartree-Fock method. Perhaps the most distinguishing feature of the xa method is the local approximation to the exchange correlation term by an approximate value proportional to the one-third power of the charge density. The significance of the one-electron energies ε<sub>i</sub> is also different in principle from those of the Hartree-Fock method. These advantages coupled with the rapid convergence of the expansion allow one to calculate molecular clusters previously intractable.

This technique (MSXα) is currently being used to study organic explosive, and related compounds. Work is now being carried out on s-N, N-dimethyl nitramine prompted by its parallelism to RDX and HMX, and on nitramide prompted by its N-N and N-O bonds. Although not yet completed some early results may be reported. For nitramide we find a total energy of

$$E_{\alpha} = -519.04 \text{ Rydbergs}$$

which may be compared to an estimated Hartree-Fock limit of

$$E(\text{HF})(\text{limit}) = -519.54 \text{ ry.}$$

and compares favorably to the much more laborious calculation result of

$$E(\text{HF}) = -519.15 \text{ ry.}$$

The xa results also predict a binding energy of -.75 ry.

The N 1s chemical shift, that is, the difference in 1s eigenvalues for the nitrogen atom associated with the nitrate group compared to the nitrogen atom associated with the di-methyl group, is experimentally determined from the solid to be 5.15 eV, whereas the xa calculation predicts, from gas phase geometry, a value of 6.4 dV.

Work is continuing on improving and extending the model in order to have a reliable tool for ascertaining the properties of interest of organic energetic materials.

*The Editors thank Mr. John G.*

*Schmidt, Special Assistant to the*

*Director, USABRL, for his help in*

*assembling the papers for this*

*issue.*

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# MARCH MEETING

## DATE:

Wednesday, March 17, 1976

## PLACE:

Knott Science Center  
The College of Notre Dame of  
Maryland  
North Charles Street

## SPEAKERS & TOPICS:

5:30 pm  
Mr. Waldemar A. Klemm  
Martin Marietta Laboratories  
"High-Temperature Reactions in  
Cement Klinker Formation"

8:30 pm  
Dr. Jan P. Skalny  
Martin Marietta Laboratories  
"Mechanism of Tricalcium Silicate  
Hydration--A New View"

## SOCIAL HOUR:

There will be a social hour after  
the meeting. Refreshments will  
be served.



Mr. WALDEMAR A. KLEMM



Dr. JAN P. SKALNY

## COCKTAILS AND DINNER:

Doyle Building Dining Room  
College of Notre Dame of Maryland

Cocktails 6:30 - 7:15 (cash bar)

Hot buffet dinner (7:15) \$5.50 per  
person. Retired chemists, students,  
and their spouses may attend the  
dinner at \$3.50 each. Reservations  
are necessary for the dinner and  
should be made no later than  
March 12 with

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It is not necessary to be a member  
of the American Chemical Society to  
attend the dinner or the talks. The  
talks may be attended without going  
to the dinner. You are invited to  
bring your spouse and friends to  
both the dinner and the meeting.

## WALDEMAR A. KLEMM

W. A. Klemm received his B.S. in chemistry from the University of California, Riverside in 1956, and his M.S. in organic chemistry from Oregon State University. His 16 years of experience in research include 10 years in portland cement-related research, and a strong background in instrumental analytical chemistry. As a Senior Research Scientist at Martin Marietta Laboratories, he is currently conducting research on high-temperature reactions of calcium silicates and aluminates.

Mr. Klemm is a member of the Transportation Research Board, the American Ceramic Society, and the American Chemical Society.

## HIGH-TEMPERATURE REACTIONS IN CEMENT CLINKER FORMATION

Today the cement industry consumes about 1% of the total energy used in the United States. The major portion of this is utilized in the high-temperature conversion of limestone, sand, and clay to the calcium silicates, aluminates and aluminoferrites which constitute the hydraulic clinker minerals found in portland cement.

The sequence of chemical reactions which occur with the introduction of raw materials to a kiln have been reasonably well characterized. It is known that with the calcination of  $\text{CaCO}_3$ ,  $\text{Ca}_2\text{SiO}_4$  is one of the first compounds formed. At temperatures above 1300 C, a liquid phase develops and  $\text{Ca}_3\text{SiO}_5$  nucleates and crystallizes from the melt. The latest data on the mechanism and kinetics of formation of the main clinker minerals and the development of the liquid phase will be discussed in relation to the properties required of a modern hydraulic binder and building material.

\*\*\*\*

## JAN P. SKALNY

Jan P. Skalny received his Dipl. Eng. (equivalent to MS) degree at the Chemicotechnological University in Prague (1958) and his Ph.D. at the Academy of Mining and Metallurgy in Cracow (1965). In 1968 he held a fellowship at Clarkson College of Technology with Professor Stephen Brunauer.

Dr. Skalny has published extensively in the fields of cement and surface chemistry. His interests are focused on the solid-liquid interactions in cementitious systems and on the high-temperature reactions in the system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  in the presence of minor components. He is actively involved in several professional societies including the American Ceramic Society (Chairman, Cements Division, 1976-77), ASTM, and the Transportation Research Board. He is a member of the Surface and Colloid Division of ACS.

## MECHANISM OF $\text{Ca}_3\text{SiO}_5$ HYDRATION - A NEW VIEW

The mechanism of hydration of  $\text{Ca}_3\text{SiO}_5$ , the most important component of commercial portland cements, will be discussed in view of the latest data obtained at Martin Marietta Laboratories.  $\text{Ca}_3\text{SiO}_5$  is known to hydrate in several stages. After a short initial reaction, there is a period of decreased reactivity (induction period), which is then followed by renewed acceleration of the reaction. Until recently, the reasons for the initiation of the induction period were ascribed to the formation of an impermeable amorphous calcium silicate hydrate coating on the unhydrated  $\text{Ca}_3\text{SiO}_5$  surface. Based on new experimental evidence, a mechanism is proposed which explains the reasons for the initiation and end of the induction period on the basis of specific adsorption of  $\text{Ca}^{2+}$  on a Si-rich surface layer, formed at the beginning of  $\text{Ca}_3\text{SiO}_5\text{-H}_2\text{O}$  interaction, and inhibition of growth of hydration products by silicate ions present in the liquid phase.



LABORATORY INVESTIGATIONS OF ATMOSPHERIC REACTIONS  
INVOLVING IONS

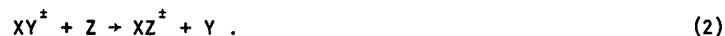
F. E. Niles and J. A. Vanderhoff  
Applied Mathematics and Science Laboratory

Near the earth's surface, the atmosphere is weakly ionized by natural radioactivity. Above this near-earth region up to an altitude of about 60 km, the atmosphere is ionized by cosmic rays. Above about 60 km, the atmosphere is ionized primarily by solar radiation. Since molecular nitrogen and molecular oxygen are the principal constituents of the earth's atmosphere, the ions initially produced by the various sources of ionization are  $N_2^+$ ,  $O_2^+$ ,  $N^+$ , and  $O^+$ . A major exception to this occurs between the altitudes of about 60 to 85 km where Lyman- $\alpha$  radiation at 121.6 nm penetrates through a small window in the oxygen absorption bands to ionize nitric oxide.

Rocket experiments utilizing mass spectrometers and other sensors have revealed that the principal positive ions below about 80 km are hydrated protons and other cluster ions. Other rocket experiments have revealed the presence of negatively charged cluster ions. The initial formation of a cluster ion is via three-body, ion-neutral association symbolically shown by



Once  $XY^+$  is formed, it can undergo another three-body, ion-neutral association reaction or a switching reaction symbolically shown by

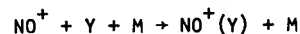


Sometimes instead of simple replacement of molecule Y by molecule Z, rearrangement of atoms can occur. Very recent studies have revealed that the cluster ions can be photodissociated as symbolically shown by



In the Aeronomy Branch of the BRL, the preceding types of reactions have been investigated utilizing three laboratory facilities; namely, (1) a stationary afterglow facility, (2) a large drift-tube facility, and (3) a small drift-tube, photodestruction facility. The stationary afterglow facility was primarily utilized to study the formation of hydrated protons and the clustering of atmospheric gases to  $NO^+$ . Some of the rate coefficients measured at 300K are given in the following table.

ROOM TEMPERATURE RATE COEFFICIENTS FOR

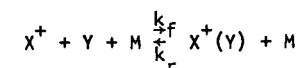


Y	M	$k(\text{cm}^6/\text{s})$	Y	M	$k(\text{cm}^6/\text{s})$
$NH_3$	NO	$(5.4 \pm 0.8)[-28]^*$	$N_2O$	$N_2O$	$(2.4 \pm 0.7)[-29]$
$SO_2$	$SO_2$	$(2.4 \pm 0.7)[-28]$	NO	NO	$(5.0 \pm 1.0)[-30]$
$H_2O$	NO	$(1.6 \pm 0.3)[-28]$	CO	CO	$(1.9 \pm 0.6)[-30]$
$H_2S$	NO	$(1.2 \pm 0.4)[-28]$	Xe	Xe	$(8.3 \pm 2.5)[-31]$
$SF_6$	$SF_6$	$(1.0 \pm 0.3)[-28]$	$N_2$	$N_2$	$(2.0 \pm 0.6)[-31]$
OCS	OCS	$(1.0 \pm 0.3)[-28]$	$O_2$	$O_2$	$(9.0 \pm 3.0)[-32]$
$CO_2$	$CO_2$	$(2.4 \pm 0.7)[-29]$	* Read as $(5.4 \pm 0.8) \times 10^{-28} \text{cm}^6/\text{s}$ .		

These measurements were made utilizing a krypton resonance lamp to ionize selectively nitric oxide in the gas mixture, mass spectrometric sampling of the ions which diffused to the wall, and signal averaging techniques. Two general trends are observed when comparing the above listed rate coefficients. Firstly, the rate coefficient increased with the number of atoms in the neutral molecule. Secondly, the rate coefficient increased with the total polarizability of the molecule with molecules possessing large permanent dipole moments having enhanced rate coefficients.

The large drift-tube facility has primarily been used to study the clustering of atmospheric molecules to the alkali ions,  $Li^+$ ,  $Na^+$ , and  $K^+$ . The alkali ions were created by thermionic emission and drifted through the atmospheric gas under the influence of a weak electric field. While drifting, the ions undergo chemical reactions and diffusion. By mass spectrometric sampling the ions arriving at the end of the drift tube, utilizing signal averaging techniques, and applying suitable data analysis, mobility coefficients and both collisional (the reverse reaction in Eq. 1) and associational (the forward reaction in Eq. 1) rate coefficients can be obtained. The rate coefficients can be obtained as a function of E/N, the ratio of electric field to neutral number density. The rate coefficients measured at an E/N of 12 Td (1 Td =  $10^{-17} \text{V cm}^2$ ) and at room temperature are given in the following table.

ALKALI-ION RATE COEFFICIENTS AT 12 Td



$X^+$	Y and M	$k_f(\text{cm}^6/\text{s})$	$k_r(\text{cm}^3/\text{s})$
$Li^+$	Ar	1.8[-31]	2.2[-13]
$Li^+$	$O_2$	1.1[-30]	3.5[-13]
$Li^+$	$N_2$	2.0[-30]	1.0[-14]
$Na^+$	$CO_2$	2.0[-29]	1.0[-14]
$K^+$	$CO_2$	4.0[-30]	2.5[-13]

The small drift-tube, photodestruction facility can be used to study either positive or negative ions and to measure photodissociation cross sections, photodetachment cross sections for detaching electrons from negative ions (sometimes photodissociation and photodetachment cannot be distinguished), mobility coefficients, and reaction rate coefficients. The facility consists of a drift tube with mass spectrometric sampling of ions, signal averaging electronics, vacuum and gas-handling equipment, and lasers to provide the specified photons. Both continuous argon and krypton ion lasers and dye lasers are employed. The laser beam is chopped and intersects the ion swarm in the drift tube just prior to the sampling orifice. At this time the spectral region between 458 and 676 nm (2.7 to 1.8 eV) has been utilized. Several interacting mechanisms affecting atmospheric ions occur in this region of the visible spectrum. A plot of the photodestruction cross sections for  $CO_3^-$  as a function of wavelength has considerable structure. Experiments have revealed that most of the photodestruction of  $CO_3^-$  results in  $O^-$ . Consequently, the observed structure has been attributed to characteristics of a bound, predissociating state. Other negative ions for which photodestruction cross sections have been measured are  $O_2^-$ ,  $O_3^-$ ,  $O_4^-$ ,  $O_2^-(H_2O)$ ,  $NO_2^-$ , and  $CO_3^-(H_2O)$ . The negative ions  $CO_4^-$ ,  $HCO_3^-$ , and  $HCO_3^-(H_2O)$  have been investigated and so far found

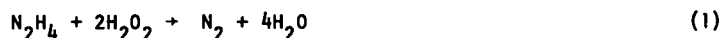
concluded on p. 11...

COPPER (II) CATALYSIS OF THE OXIDATION OF  
HYDRAZINE BY HYDROGEN PEROXIDE

J. Richard Ward  
Interior Ballistics Laboratory

Corey, Mock, and Pasto (1961) recently reported that hydrazine can react with either hydrogen peroxide or oxygen to form diimide which can then hydrogenate olefins. The reaction proceeds at a measurable rate in the presence of trace amounts of copper (II), but the reaction is suppressed by the addition of ethylenediaminetetraacetic acid (EDTA). A review of the literature revealed that Sigel and coworkers (1968, 1969) examined the kinetics of the oxidation of hydrazine by hydrogen peroxide, catalyzed by 2,2-dipyridyl copper (II), but attempts to measure the kinetics in the presence of hydrated copper (II) were unsuccessful due to precipitation of copper oxide. The kinetics have been reexamined in the presence of sufficiently small quantities of copper (II) to avoid precipitation of copper oxide.

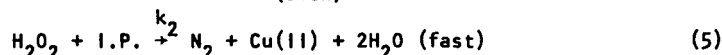
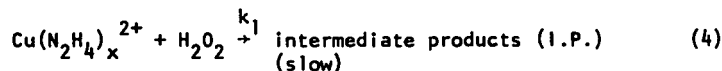
The stoichiometry of oxidation of hydrazine by hydrogen peroxide in aqueous solution is as follows:



The rate of the reaction may be followed by monitoring the rate of formation of nitrogen. In the presence of EDTA there is virtually no reaction. In the presence of small amounts of copper (II) ( $10^{-6}\text{M}$ ) the rate of reaction was found to be

$$\frac{d[\text{N}_2]}{dt} = k_{\text{obs}} [\text{H}_2\text{O}_2] [\text{Cu(II)}] \quad (2)$$

The reaction is seen to be first order in hydrogen peroxide and copper (II), but the rate is independent of the concentration of hydrazine. A mechanism consistent with the above observations is shown below



The rate law for such a mechanism reduces to

$$\frac{d[\text{N}_2]}{dt} = \frac{k_1 k_2 [\text{N}_2\text{H}_4] [\text{H}_2\text{O}_2] [\text{Cu(II)}]_T}{1 + K[\text{N}_2\text{H}_4]} \quad (6)$$

Since the equilibrium constant,  $K$ , is of the order of  $10^4$ ,  $K[\text{N}_2\text{H}_4]$  is much greater than 1 which makes Eq. (6) reduce to the experimentally observed rate law, Eq. (2). From the known concentrations of copper (II) and hydrogen peroxide,  $k_1$  is  $2 \times 10^2 \text{M}^{-1} \text{sec}^{-1}$ .

The chemical significance of this is that hydrazine itself is stable in the presence of hydrogen peroxide. When complexed by copper (II), the hydrazine virtually instantaneously reacts with the hydrogen peroxide. It is not clear why this should be so. The presence of diimide ( $\text{N}_2\text{H}_2$ ) inferred from Corey's results suggests that Eq. (3) proceeds by hydrogen atom transfer from complexed hydrazine to hydrogen peroxide. Somehow the presence of the copper (II) coordinated to hydrazine makes such a process much more facile than for pure hydrazine.

Since hydrazine has a long history as a liquid propellant, the condensed phase reactions important in the combustion process may be influenced by similar considerations. In terms of long-term storage of hydrazine, it would appear to be important to keep metal ions such as copper away from hydrazine, since oxygen, a two-electron oxidizer like hydrogen peroxide, should oxidize hydrazine by a similar mechanism.

*continued from p. 9...*

to have zero or very small cross sections. The photodissociation cross sections for the positive ions  $\text{O}_4^+$ ,  $\text{O}_2^+(\text{H}_2\text{O})$ , and  $\text{O}_2^+(\text{CO}_2)$  have been measured. For  $\text{O}_2^+(\text{CO}_2)$ , the product ion  $\text{CO}_2^+$  was detected. From these observations and measurements, limits on the binding energies of the cluster ions and the photodestruction frequency by solar photons or by other photon sources may be determined.

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