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"CHEMICAL EFFECTS OF THE NUCLEAR REACTION $N^{14}(n,p)C^{14}$
IN VARIOUS NITROGENOUS COMPOUNDS"

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Enclosures:

Final Report No. COO-1620-7, entitled "Chemical Effects of the Nuclear Reaction $N^{14}(n,p)C^{14}$ in Various Nitrogenous Compounds" (2)
Reprint No. COO-1620-4, entitled "The Kinetics of Deuteration of Pyrazole" (4)
Reprint No. COO-1620-5, entitled "The Kinetics of Deuteration of Imidazole" (4)

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I. CARBON HOT ATOM CHEMISTRY

A. Introduction

When compounds containing nitrogen are subjected to thermal neutron irradiation, the following nuclear reaction occurs:

The recoil energy of the product C^{14} atom is 40 Kev., about 10^4 times chemical bond energies. This large recoil energy ensures rupture of all residual chemical bonds, i.e., chemical bonds originally attached to N^{14} . The recoiling C^{14} atom may then enter chemical combination after dissipating most of its kinetic energy through collisional interactions with atoms, ions, or molecules of the target material. This nuclear reaction and others that produce radioactive carbon provide unique ways to study the chemistry of atomic carbon under varying environmental conditions. The possible chemical combinations of the recoil atom depend initially upon the atomic and molecular constitution of the target and its state of aggregation.¹⁻¹² The ultimate distribution of labeled products depends as well upon pre- and post-irradiation treatment of the target,^{6-8,12} and upon concomitant radiation attending target irradiation.^{13,14}

In the case of the $\text{N}^{14}(\text{n},\text{p})\text{C}^{14}$ nuclear reaction, long periods of thermal neutron irradiation of the nitrogenous target are required to produce sufficient radioactivity in long-lived C^{14} .

Such long periods of irradiation enhance the probability that radiation may affect the chemical fate of the recoil atom. Because of reduced diffusion, the effect of radiation is less for solid than for liquid and gaseous targets,^{6,13-15} For this reason, studies of C^{14} recoil chemistry are usually restricted to solids.

Labeled products in target crystals can be released from the target by (1) dissolution in solvent, (2) volatilization of the target, and, if the target is thermally unstable, (3) volatilization by thermal decomposition of the target.⁸ Dissolution of target crystals introduces the possibility that secondary reactions between crystal-entrapped recoil products and solvent may obscure the identity of these entrapped products. Similarly, the temperature increase attending target volatilization or decomposition may promote further reaction of the original entrapped species with atoms, ions, or molecules of the target material. However, a combination of solvent dissolution and target volatilization (or decomposition) together with thermal anneal techniques¹⁶ provides valuable information on the nature of the labeled entities confined within the solid.^{6,7}

1. Historical Background

(a) Ammonia and Salts of Ammonia.

Wolf and co-workers at Brookhaven studied the hot atom chemistry of carbon in gaseous NH_3 resulting from recoiling C^{14} and C^{11} atoms. The expressed purpose of these workers was to

determine the entire product distribution of the recoil atom in the target. Yang and Wolf¹¹ subjected NH_3 to thermal neutrons in the Brookhaven reactor, then determined the C^{14} products by radio-gas chromatography. C^{14}H_4 was the principal product, accompanied by a small yield of $\text{C}^{14}\text{H}_3\text{NH}_2$. Cacace and Wolf^{13,14} determined the C^{11} -labeled compound distribution produced in NH_3 by the $\text{N}^{14}(\text{p},\alpha)\text{C}^{11}$ reaction. The fraction of C^{11}H_4 grew at the expense of $\text{C}^{11}\text{H}_3\text{NH}_2$ with increased dose of protons; at a dose of 0.1 ev/molecule, the distribution was 45% C^{11}H_4 , 35% $\text{C}^{11}\text{H}_3\text{NH}_2$, and 20% $\text{C}^{11}\text{H}_2\text{NH}$ (methylenimine), but at a dose of > 0.1 ev/molecule, labeled methane was essentially the only product. The increase in methane with increased dose was attributed to radiolytic conversion in the proton beam. Cacace and Wolf concluded that methylamine and methylenimine are produced by hot reactions in ammonia, and that methane is produced in both thermal reactions and radiolytic reaction.

Yankwich and Vaughan¹ and Yankwich and Marteney¹² studied the chemistry of C^{14} produced in crystalline ammonium halides. The distribution of labeled products provides an interesting parallel with that of C^{11} in low dose proton irradiated solid ammonia.¹⁴ The yields of methylamine were 79% and 75% in ammonium bromide¹ and solid ammonia, respectively, and the yields of methane were 7.5% and 9% for these targets, respectively. In addition, formaldehyde (6%) was found when the crystalline ammonium bromide was dissolved in water, which suggests that methylenimine could have been the

precursor in the crystals prior to their dissolution.¹ This parallel supports the contention that the radiolytic effect upon the distribution of labeled products is diffusion controlled, and that this diffusion is of negligible consequence in high melting ionic salts. Yankwich and Cornman² discovered the same labeled products in ammonium sulfate that were found in the ammonium halides. The yield of oxygen-containing products was markedly higher in the sulfate, because of oxygen in the target. Thus, there was 40% $C^{14}O_2$, 16% $HC^{14}OOH$, 13% $HC^{14}HO$, but only 16% $C^{14}H_3NH_2$. In addition, urea was found to be 7% in the sulfate, compared to < 1% in the halides. The large yield of oxygen-containing labeled C^{14} products attests to the effective scavenging capability of lattice oxygen.²

(b) Salts of Hydrazine.

Vaughan, Lieu, and Bugay investigated the chemistry of C^{14} in crystalline hydrazinium sulfate⁵ and hydrazinium chloride.¹⁷ Large yields of cyanamide, methylamine, guanidine, urea, cyanic acid, and possibly formamidine and methyleneimine (or methylenediamine) were found. The richer spectrum of labeled nitrogen-containing compounds in the salts of hydrazine compared to that in the salts of ammonia was attributed to the weak N-N link in the $N_2H_6^{++}$ ion.⁵

(c) Metal Nitrides.

Yankwich and Cornman reported research on C^{14} recoil chemistry in Be_3N_2 ,³ and Kuhry and Adloff on a series of metal

nitrides.^{9,10} The most definitive investigation of the system was that of Finn, Ache, and Wolf on Mg_3N_2 .⁶ This target dissolved in 2 N NaOH yielded 41% $\text{C}^{14}\text{N}_2^-$, 18% C^{14}N^- , 12% C^{14}H_4 , 9% $\text{C}^{14}\text{H}_2\text{NH}$, and essentially no $\text{C}^{14}\text{H}_3\text{NH}_2$. Thermal anneal of the irradiated target at 500° for five days yielded a dramatic increase in $\text{C}^{14}\text{H}_2\text{NH}$ (to 66%), an increase in C^{14}H_4 (to 23%), but large decreases in $\text{C}^{14}\text{N}_2^-$ and C^{14}N^- . These changes attending thermal anneal were attributed to alterations of C^{14} to N bond distances during anneal, leading to increased susceptibility of reaction with solvent to form methyleneimine.⁶ Stöcklin and Vogelbruch⁸ determined the labeled products resulting from thermal decomposition of n-irradiated Cu_3N in the presence of hydrocarbons or iodohydrocarbons; C^{14}O_2 was the major product despite careful pre-irradiation outgassing. Various C^{14} -labeled nitriles were prepared; for example, the yield of cyanobenzene produced by decomposition of Cu_3N in an atmosphere of iodobenzene was about 10%.⁸

B. C^{14} Hot Atom Chemistry in Alkali Azides

1. Introduction.

The purpose of the research on alkali azides was to study the detailed chemistry of the recoil C^{14} atom in these crystalline targets. As in related investigations, the experimental approach was to determine the identities and relative amounts of the labeled products resulting from the nuclear transformation $\text{N}^{14}(\text{n},\text{p})\text{C}^{14}$.

The alkali azides were chosen for this investigation for the

following reasons (1) only two elements (alkali metal and nitrogen) constitute the target, simplifying the radiocarbon product distribution, and hence, interpretation of the results; (2) alkali azides are readily soluble in water and other solvents; (3) alkali azides decompose at relatively low temperatures, providing an alternative to solvent dissolution to release entrapped labeled products; (4) the radiation chemistry of NaN_3 and KN_3 in the thermal column of a nuclear reactor has been reported,¹⁸ making it possible to estimate the effect of reactor radiation upon the radiocarbon product distribution.

The two targets used in this investigation, NaN_3 and KN_3 , are white, crystalline solids. Sodium azide crystals are body-centered rhombohedral, that decompose slowly without melting at 275° to $\text{Na}_{(s)}$ and $\text{N}_{2(g)}$.¹⁹ Potassium azide crystals are body-centered tetragonal that melt at 350° ; the molten salt decomposes slowly at 355° to $\text{K}_{(s)}$ and $\text{N}_{2(g)}$.^{20,21}

2. Experimental.

(a) Target Irradiation.

Sodium and potassium azides obtained from Eastman Organic Chemicals were each recrystallized three times in water,¹⁹ then oven dried at 110° . Ten gram samples of each were placed within necked quartz ampoules, heated under vacuum for one hour at 220° , then sealed off under helium at ambient pressure. The specimens were irradiated in the thermal column of the Los Alamos

Omega West Reactor for 113 hours in a neutron flux of $\sim 5 \times 10^{11}$ n $\text{cm}^{-2} \text{sec}^{-1}$ (integrated flux $\sim 1.5 \times 10^{17}$ n cm^{-2}); the ambient temperature in the thermal column was between 60° and 70°. The ampoules were opened in a dry box and stored under helium between experiments. Preliminary operations such as sample weighings were made in the dry box.

(b) Aqueous Dissolution of Target Samples.

All aqueous dissolutions were carried out in neutral to weakly alkaline media (*i.e.*, aqueous KN_3 is weakly alkaline). Target samples (KN_3 or NaN_3) weighing 0.01 g to 0.05 g were dissolved in doubly distilled water; carriers were added either in aqueous solution or as gases preparatory to separation and radio analysis. In general, no more than four carriers were added and separated in a given experiment (see ref 5). The aqueous solution of the target and carriers was adjusted to 100 ml prior to the initiation of separation procedures.

(c) Dissolution of Sodium Azide Target Samples in Anhydrous Hydrazine.

Anhydrous hydrazine was prepared by the procedure of Hale and Shetterly;²² Eastman Organic Chemicals hydrazine (95+%) was distilled from calcium oxide under reduced pressure. Sodium azide samples of about 0.03 g each were dissolved in 1 ml of hydrazine, after which carriers in aqueous solution were added. Excess 6 M H_2SO_4 followed by 95% ethanol was added to the now

aqueous solution to remove hydrazine as hydrazinium sulfate. The filtrate volume was adjusted to 100 ml prior to separation of carriers.

(d) Cyanide, Cyanamide, and Hydrolyzable Activities.

A solution containing dissolved target, KCN, and cyanamide was divided into equal aliquots. Aliquot 1 was acidified with 1 M nitric acid; excess aqueous 1 M AgNO₃ was added to precipitate AgCN. The solution was filtered and the precipitate discarded. The filtrate was made alkaline with 3 M NH₄OH, causing silver cyanamide (Ag₂CN₂) to precipitate. This precipitate was collected and dissolved in 6 M H₂SO₄, then the acid solution was neutralized with 3 M NH₄OH to reprecipitate Ag₂CN₂. The cycling of the cyanamide ion (CN₂⁼) precipitation is a purifying procedure.³ The dried Ag₂CN₂ was combusted over copper oxide at 800° to yield CO₂; the CO₂ was collected as BaCO₃. A stream of air was swept through aliquot 2 through an acidified 1 M AgNO₃ solution and on into a 1 M NaOH solution. Aliquot 2 was acidified with dilute H₂SO₄, then warmed, causing HCN to distill into the AgNO₃ solution precipitating AgCN. Carbonate activity resulting from dissolved CO₂ or from acid hydrolysis was caught in the NaOH solution. The dried AgCN was combusted over copper oxide. Gaseous CO₂ introduced into the air stream served as a carrier for the hydrolyzable activity. Both cyanide and hydrolyzable fractions were collected as BaCO₃.

(e) Methylamine.

An aqueous solution containing target, methylamine carrier, and excess sodium hydroxide was distilled. The distillate was condensed into saturated aqueous picric acid. The methylamine picrate derivative was recrystallized from water, combusted over copper oxide, and collected as BaCO_3 . A preliminary experiment indicated that guanidine does not distill over to form guanidine picrate.

(f) Methyleneimine.

A solution containing target and formaldehyde carrier in a closed pressure compensated system was made 7 N in H_2SO_4 ,⁶ then refluxed for one hour. The methone derivative of formaldehyde¹ was prepared, recrystallized from aqueous ethanol, then converted to BaCO_3 .

(g) Formaldehyde, Formic Acid, and Guanidine.

Formaldehyde was separated as the methone derivative,¹ formic acid was determined by the specific mercuric acetate oxidation to CO_2 ,¹ and guanidine was separated as the picrate derivative. All fractions were converted to BaCO_3 .

(h) Urea.

The oxalate derivative of urea⁶ was prepared, recrystallized from water, then converted to BaCO_3 .

(i) Gases.

Low boiling carrier-free gases were separated chromatographically using the F and M Model 700 gas chromatograph. The

following columns were used; Silica gel (CO_2 and CH_4); 5A molecular sieve (CO_2 , CO , and CH_4); 20% Di-(2-ethylhexyl) Sebacate on celite (HCN and CH_3CN).

(j) Thermal Anneal.

Samples of target (KN_3) were heated under vacuum at 300° for periods ranging from one to ten hours in a temperature-regulated Lindberg Hevi-Duty furnace.

(k) Thermal Decomposition.

Samples of target were heated in a glass or quartz tube projecting into the Lindberg furnace; the glass tube was used for decompositions carried out at 400° , and the quartz tube was used for higher temperatures. The decomposition tubes were connected to a U-tube cold trap (-195°) which was connected to the vacuum line. In some instances, decompositions under vacuum were conducted. For decompositions in hydrogen and oxygen atmospheres, the gas was metered into the previously evacuated system prior to heating until a pressure of one-half atmosphere was reached. For decompositions in an iodomethane atmosphere, a weighed amount of CH_3I in a quartz thimble was placed within the decomposition tube that contained the target sample in a separate thimble. The amount of CH_3I was that calculated to be equivalent to about one-half atmosphere at 500° . The CH_3I was cooled to -195° , and the system evacuated, then allowed to warm up and evaporate. This cyclic process of freezing with evacuation followed by warming and evaporation was carried out to

remove air oxygen from the CH_3I . After these purification steps, the decomposition tube was inserted into the hot Lindberg furnace. For decompositions in a water vapor atmosphere, a procedure similar to that used for iodomethane was followed. When KN_3 was the target being decomposed, the decomposition tube was held at 400° for three hours. In a control experiment, decomposition of 0.07 g of irradiated KN_3 was complete within two hours. For NaN_3 decompositions at 500° , heating was continued for one hour or for three hours, but for NaN_3 decompositions at 500° , five minutes of heating was more than adequate. After decomposition, carrier-free volatile products in the U-tube trap were transferred to a flow injector²³ then injected into the gas chromatograph for separation. The decomposition tube was washed with water which dissolved nonvolatile products of the decomposition. Appropriate carriers in aqueous solution were added to the wash solution prior to chemical separation.

(1) Radioactivity Determinations.

In most instances, labeled products were separated with carriers, then converted to BaCO_3 prior to counting. CO_2 evolutes from the various BaCO_3 specimens were counted in batch proportional counters^{24,25} with methane or P-gas as the counter gases. Some of the CO_2 evolutes were counted in an ionization chamber using the Cary 31 vibrating reed electrometer. Radioactivity determinations were computed on the basis of total recovered BaCO_3 for each carrier, necessitating no correction for carbonate blank. In some instances, volatile carrier-free products separated gas chromatographically

were counted in a flow sandwich-type proportional counter²⁵ following elution from the gas chromatograph.

(m) Total Target Specific Activity.

The total C^{14} activity per gram of irradiated KN_3 was determined by alkaline permanganate oxidation to carbonate; aqueous KCN was added to the solution containing the target sample to provide weighable carbonate. During reflux, a CO_2 -free stream of air swept volatile or gaseous compounds over copper oxide at 800° . The air stream passed through a bubbler trap containing 1 M NaOH. After refluxing one hour, the permanganate solution was acidified with excess H_2SO_4 , and the carbon dioxide product was caught in the aqueous NaOH bubbler. The total activity per gram of KN_3 determined in two runs was $3,087,000 \pm 28,000 \text{ counts min}^{-1} \text{g}^{-1}$. The total specific activity of NaN_3 was determined by the same procedure. The total activity per gram of NaN_3 determined in three runs was $1,505,000 \pm 4,000 \text{ counts min}^{-1} \text{g}^{-1}$.

3. Results.

(a) Potassium Azide.

The results of experiments in irradiated KN_3 can be categorized according to the mode of release of the C^{14} -labeled entities from the target crystals. In the first category, target samples were dissolved in water. In the second class, target samples were melted.

i. Aqueous Dissolution

Table I gives the distribution of the recoil atom (C^{14}) among products for target samples subjected to no post-irradiation annealing. The products listed in Table I account for ~100% of the total C^{14} radioactivity produced in the target; the activity attributed to CO_2 is also part of that attributed to Hydrolyzable. The results of aqueous dissolution on post-irradiation thermally annealed samples are shown in Figure 1. Not shown in Figure 1 is the effect of thermal anneal upon the yield of methylamine. Heating of irradiated KN_3 for one hour at 300° reduced the yield of $C^{14}H_3NH_2$ from 25% to 0%

ii. Disolution in Melt, Followed by Partial or Complete Thermal Decomposition.

Table II gives the results of experiments in which the target samples were first melted (350°) then heated at 400° until the target entirely decomposed (3 hours). In run 9, the decomposition residue was analyzed for methylamine (i.e., as a salt) and guanidine; neither was found. In run 4, parallel runs were made for cyanamide ion, with the indicated good agreement. In runs 10 and 11, the target samples were melted, but quenched before decomposition was complete. The heating time in run 10 was only five minutes; the $C^{14}N^-$ yield was 49.2% and the $C^{14}N_2^-$ was 29.2%, not markedly different from yields with aqueous dissolution of unannealed target. In run 11, a sample held at 400° for one hour gave 30.0%

Table I
~~Table I~~

C^{14} -Labeled Products: Aqueous Dissolution of n-Irradiated
 KN_3 Not Subjected to Thermal Annealing.

Compound	Number of Separate Determinations	Total Activity (%)
$C^{14}N^-$	3	45.7 ± 0.7
$C^{14}N_2^-$	5	17.0 ± 0.6
$C^{14}H_3NH_2$	6	24.8 ± 1.0
$HC^{14}OOH$	1	~ 2.1
$C^{14}O(NH_2)_2$	3	4.4 ± 1.0
$C^{14}H_4 + C^{14}O^a$	3	3.8 ± 1.1
$C^{14}H_2NH$	1	<1
$C^{14}H_2O$	1	<1
$C^{14}NH(NH_2)_2$	1	0
$C^{14}O_2$	1	~ 1.5
Hydrolyzable	3	3.2 ± 1.4

^a Obtained by combustion of combined carriers over
 CuO at 800°

KEY: $\circ$ CN_2^-
 $\square$ CN^-
 ∇ CO_3^{2-} (Hydrolyzable)

FIGURE 1: EFFECT OF POST-IRRADIATION ANNEALING AT 300° UPON C^{14} -PRODUCT DISTRIBUTION

Table II. C^{14} -Labeled Products: Thermal Decomposition
of n-Irradiated KN_3 at 400° ; 3 Hours

Compound	Total Activity (%)								Average
	1	2	3	4	5	6	7	8	
CN_2^-	75.4	66.5	68.8	87.2 86.0	93.0	88.0	84.0	89.0	88.0
CN^-	2.8	1.5	4.1	--	--	--	--	--	2.8
Hydrolyzable	3.0	1.1							1.6
Cold Trap ^a	0	0	0						0
TS ^b		94.8	96.5						95.7

^a -195°

^b Total Solution Components, obtained by alkaline permanganate combustion of an aliquot of the dissolved decomposition residue.

$C^{14}N^-$ and 61.7% $C^{14}N_2^-$. It is clear from runs 10 and 11 that $C^{14}N^-$ is transformed gradually in the melt to $C^{14}N_2^-$.

(b) Sodium Azide.

Like KN_3 , the experiments on irradiated NaN_3 can be categorized according to the way in which the labeled products are released from the crystal structure. First, aqueous dissolution, second, dissolution in anhydrous hydrazine, and third, thermal decomposition without melting.

i. Aqueous Dissolution.

The results of aqueous dissolution are given in Table III.

Table III
~~Table III~~

C^{14} -Labeled Products: Aqueous Dissolution of
n-Irradiated NaN_3 Not Subjected to Thermal Annealing.

Compound	Number of Separate Determinations	Total Activity (%)
$C^{14}N^-$	3	74.8 ± 1.2^b
$C^{14}N_2^-$	3	14.5 ± 1.0
$C^{14}H_3NH_2$	5	19.0 ± 1.7
Hydrolyzable	2	~ 0.4
$CH_4 + CO$ ^a	3	~ 0.4

^a Obtained by combustion of combined carriers
over CuO at 800° .

Because NaN_3 decomposes at a lower temperature than does KN_3 , a detailed post-irradiation annealing study was not made for NaN_3 . In one experiment, however, irradiated NaN_3 was held at 300° for five hours. The target sample did not decompose during this interval, but undoubtedly did undergo partial decomposition at the surface of the crystals.¹⁹ The yields of $C^{14}N_2^-$, $C^{14}N^-$, and Hydrolyzable were 72.6%, 13.4%, and 5.7%, in very close agreement with yields observed for these products in irradiated KN_3 annealed for five hours at 300° (see Figure 1).

ii. Dissolution in Anhydrous Hydrazine.

The results of these experiments are shown in Table IV.

Table IV

C^{14} -Labeled Products: Dissolution of
n-Irradiated NaN_3 in Anhydrous Hydrazine

Compound	Number of Separate Determinations	Total Activity (%)
$C^{14}N^-$	2	93.0 ± 4.3
$C^{14}N_2^-$	2	14.2 ± 0.1
$C^{14}H_3NH_2$	2	< 0.2
Hydrolyzable	2	~ 0.8

It is clear by comparing Tables III and IV that the C^{14} activity that appears as methylamine when water is the solvent appears instead in the cyanide fraction when hydrazine is the solvent.

iii. Thermal Decomposition in Vacuo.

The product distributions resulting from thermal decomposition of n-irradiated NaN_3 under vacuum are given in Table V. At 400° , cyanamide was essentially the only product, but at higher temperatures the yield of cyanide increased relative to that of

cyanamide. No volatile activity was recovered. Thus, the so-called Hydrolyzable activity was probably either labeled carbonate or cyanate, not carbon dioxide.

Table V
~~~~~

C^{14} -Labeled Products: Thermal Decomposition of n-Irradiated NaN_3 in a Vacuum.

Temperature	Time of Heat Application	Total Activity (%)		
		$C^{14}N^-$	$C^{14}N_2^+$	Hydrolyzable
400°	1 hour ^a	2.0 ±0.2	90.8 ±2.6	~0.1
400°	2 hours ^a	1.8 ±0.2	97.8 ±2.1	~0.2
500°	5 minutes ^b	28.2	65.4	~0.2
900°	5 minutes ^c	22	25	3

^a Two runs

^b One run. Decomposition occurred with light emission; was complete after two minutes.

^c One run. The remaining 50% of the activity was trapped, together with metallic sodium, within the quartz structure. The trapped activity could be released by strong, prolonged heating.

iv. Thermal Decomposition in Various Gaseous Atmospheres.

These decompositions were carried out at 500° for five minutes in the presence of a foreign gas exerting about one-half atmosphere pressure. The results are given in Table VI. The

Table VI

C^{14} -Labeled Products: Thermal Decomposition of n-Irradiated NaN_3 in Various Gaseous Atmospheres: 500° , $\frac{1}{2}$ Atmosphere.

Gas	Total Activity (%) ^a			
	$C^{14}N^-$	$C^{14}N_2^-$	Hydrolyzable ^b	Other
H ₂	31.5	65.0	0.0	$C^{14}H_4$: 0.0
O ₂	0.0	0.0	97.5	$C^{14}O$: 0.0
CH ₃ I	23	37	1	CH ₃ $C^{14}N$: ~12 Gas w/BP < -78°: ~1 Tar: ~10
H ₂ O	0.7	1.6	84	Volatile gases: 0.0

^a $\pm 10\%$ or less

^b Recovered from decomposition residue upon aqueous acidification.

activity accounted for in the runs were 96.5% of the total for H₂, 97.5% for O₂, 84% for CH₃I, and 86% for H₂O. The yields of labeled products were the same for decompositions in the hydrogen atmosphere and in a vacuum. That is there was no reaction between H₂ and C^{14} -entities emerging at the surface of decomposing NaN_3 crystals. By contrast, O₂⁸ and H₂O proved to be extremely effective scavengers, causing essentially complete transformation of all C^{14} -entities to

Na_2CO_3 . Iodomethane apparently reacted with ca. 30% of the available C^{14} , producing chiefly labeled acetonitrile and tarry residue.

4. Discussion.

The recoiling C^{14} atom leaves the site of the nuclear event with kinetic energy of 40 keV, most of which it must lose through ionization, electronic excitation, and finally elastic collision before it may enter stable chemical combination.^{4,16} Recent experimental evidence²⁶ indicates that a recoil atom must stop in a very short time (pico seconds) and that the rate of dissipation of the energy from the terminal hot zone¹⁶ depends upon the insulating properties of the target matter. Therefore, the temperature in the hot zone depends upon the thermal conductivity of the medium. Thus, in a metal foil, the hot zone will exhibit lower temperatures than in an ionic solid, because the energy loss from the hot zone in the foil will be much more rapid. Finn, Ache, and Wolf⁶ estimated that the maximum hot zone temperature could be 2500°K for ca. 10^{-11} seconds for C^{14} recoils in ionic solids. If such high temperatures occur in hot zones in irradiated alkali azides, local decomposition of the salt would begin, so that the slowed C^{14} atom could react with highly excited azide ions,²⁰ nitrogen molecules, nitrogen atoms,²⁰ and possibly alkali metal atoms. Quenching of the hot zone due to rapid cooling could stop some or all of the reactions of the recoil atom short of completion, leaving it in an activated (metastable) chemical combination. Dissolution of the irradiated

solid in solvent could then lead to vigorous reactions between the metastable combinations ("precursors") and the solvent to produce secondary or post-dissolution products. If the target is thermally annealed before dissolution, enabling precursors to react further within the crystal,¹⁶ a different spectrum of labeled products would result.

The product distributions observed for alkali azide targets conform well to the above model. Thus, methylamine (Table I and III) is a post-dissolution product of a precursor and water. Since dissolution of irradiated NaN_3 in hydrazine yielded no methylamine, but instead to commensurately increased cyanide ion (Tables III and IV), the precursors for cyanide ion and methylamine could be similar. One possibility would be that most of the C^{14} atoms are combined with one nitrogen atom, probably as an ion. In the unannealed crystals, the bonds could range from the most stable length (1.13 Å in KCN) to slightly longer lengths.⁶ When a target sample dissolves in water, these combinations with bond lengths longer than a certain critical value would react with water to yield $\text{C}^{14}\text{H}_3\text{NH}_2$, while the remaining combinations resist attack by water. In irradiated KN_3 , about 36% of the precursors would have sufficiently long bonds to react with water to produce methylamine, while in NaN_3 , about 27% would. It is clear that the methylamine precursors must be highly activated in order to undergo five-fold protonation. When a sample dissolves in hydrazine, this excess energy could be dissipated

in inelastic and elastic collisions not leading to chemical change. Since thermal anneal processes tend to correct defects in lattice structure, the process should favor C^{14} entities most like lattice ions, i.e., N_3^- . Both azide and cyanamide ions are linear, each with two equivalent bonds of $1.16 \text{ \AA}$.²⁷ Hence, azide ion sites could be occupied by cyanamide ions without strain. The large yields of $C^{14}N_2^-$ attending long-term anneal of irradiated KN_3 supports this viewpoint. Annealing could cause displaced azide ions to react with cyanide ion to produce CN_2^- ions with C-N bond lengths of $1.16 \text{ \AA}$. The increased yield of Hydrolyzable activity after three or four hours (Figure 1) could be due to the formation of cyanic acid ($HOC^{14}N$) upon dissolution of the target in water. The precursor of $HOCN$ could be an intermediate in the chemical change of $C^{14}N^-$ to $C^{14}N_2^-$, with C-N bond length appropriate to the path leading to $HOC^{14}N$. With longer anneal than four hours, the intermediate would be converted to cyanamide. After one hour of anneal of irradiated KN_3 , no CH_3NH_2 was found when the target was dissolved in water. One hour of anneal may be sufficient to relieve the strain on the methylamine precursor, permitting it to revert to $C^{14}N^-$ or perhaps to react with N_3^- to produce $C^{14}N_2^-$.

When KN_3 is heated to 400° , it melts rapidly, then the melt begins to decompose. Thus, when irradiated KN_3 is heated and held at 400° , the labeled precursors when freed from the crystal restraint encounter principally N_3^- and K^+ ions. The large yields

of $C^{14}N_2^=$ that result from the melting and subsequent decomposition of the KN_3 target can therefore be attributed to the reaction between cyanide and azide ions in the hot melt:

However, when NaN_3 is heated to 400° or higher, decomposition occurs at the surface;^{19,20} the precursors continually being exposed at the surface can react with highly activated azide ions, N_2 , K, and/or molecules of gas in the surrounding atmosphere. In vacuo at 400° , $C^{14}N_2^=$ is essentially the only product (Table V). At this temperature, there appears to be adequate time for the $C^{14}N^-$ to react with azide either at the surface or within the crystal to produce $C^{14}N_2^=$. When irradiated NaN_3 is heated to 500° (or higher) decomposition occurs rapidly, apparently sufficiently so that the transformation of $C^{14}N^-$ to $C^{14}N_2^=$ is not complete. In a hydrogen atmosphere at 500° , the precursors do not react with H_2 at all. However, in oxygen, reaction between precursors and O_2 is complete. Since the decomposition of NaN_3 is exothermic,²⁰ the temperature at the surface is likely well above 500° , so that combustion of the precursors is likely. Water also behaves as an oxidizing scavenger at high temperature, in contrast to its behavior as a reducing medium at room temperature. The only product of interest in iodomethane atmosphere is $CH_3C^{14}N$ (12%, Table VI). Here, a methyl radical could transfer an electron to atomic sodium, then combine with a $C^{14}N^-$ ion to yield labeled acetonitrile.

Cunningham¹⁸ determined reactor radiation-induced decomposition of NaN_3 and KN_3 in a thermal column, under conditions similar to the target irradiations in this research. In thermal columns, γ -radiation is attributable principally to neutron capture by carbon in the graphite moderator. In the research by Cunningham, the alkali azide targets were subjected to integrated flux of 10^{18} n cm^{-2} , compared to that in our study of 15×10^{17} n cm^{-2} . The percent decomposition of target samples found by Cunningham was only 0.03%. Since the rates of reactions between recoil atom precursors and radiolytically produced species are diffusion controlled in crystalline targets,¹³ the contribution of radiation chemical effects to the recoil product distribution would be negligible in alkali azide targets. This conclusion is in agreement with the experimental observation of Finn, Ache, and Wolf in their magnesium nitride target.⁶

C. C^{14} Hot Atom Chemistry in Tetrazole

1. Introduction.

This investigation was inspired by the research of Rose, McKay, and Wolfgang on C^{11} labeling produced by the nuclear reaction $\text{C}^{12}(\gamma, n)\text{C}^{11}$ in cyclopentadiene.²⁸ The chief products found were benzene (8.6%), acetylene (10%), diacetylene (8.9%), vinylacetylene (3.8%), fulvene (3.0%), and polymer (59.0%). Benzene was assumed to result from insertion of the recoil atom into a $\text{C}=\text{C}$ bond. The

purpose of our investigation on tetrazole (I) was to determine

(1) the yield of labeled s-tetrazine, and (2) the yields of labeled five-member heterocycles. In addition, tetrazole is an interesting target for neutron irradiation because of its large ratio of N to C, its ready solubility in water and other solvents, and its tendency to sublime. Thus, labeled products in the target can be released via dissolution or volatilization. Other investigations of C^{11} or C^{14} labeling of complex organic molecules have been described in a review by Wolf,²⁹ and in subsequent papers by Wolf and co-workers and Wolfgang and co-workers.

2. Experimental.

(a) Target Irradiation.

Aldrich Organic Chemicals Tetrazole was recrystallized two times from ethyl acetate, and oven dried at 120° for three hours. Two specimens, of one gram and sixth tenths gram, respectively, in separate quartz ampoules were subjected to high vacuum for four hours, then sealed off under ambient helium pressure. The specimens were irradiated in the thermal column of the Los Alamos Omega West Reactor for fourteen hours in a neutron flux of $\sim 3 \times 10^{12}$ n $\text{cm}^{-2} \text{ sec}^{-1}$. The ampoules were opened in air, the contents transferred

to weighing bottles, and the bottles stored within a vacuum desiccator. Subsequent transfers of samples of target were carried out under a flow of helium gas.

(b) Gas Chromatographic Separations.

Samples of irradiated tetrazole were funneled into dried capillary tubes. These tubes were weighed, then held under high vacuum for several hours before being sealed off in a flame. The sealed capillaries were inserted into the Hewlett-Packard solid injector of the F and M gas chromatograph, held at 170° for ten minutes, then injected into the input column of the chromatograph. Eluted compounds were trapped in cold traps at -195° , then oxidized to CO_2 by sweeping them over copper oxide at 800° ; the CO_2 was trapped in aqueous NaOH which already contained a known quantity of Na_2CO_3 . The compounds were collected in the form of BaCO_3 .

i. Total Volatile Fraction.

A dry, empty, two-foot glass column was used for this separation. The flow rate was 100 cc min^{-1} and the oven temperature was 90° . Effluents that passed through the column within 15 minutes were defined to be the Total Volatile Fraction.

ii. Carbon Dioxide.

A six-foot steel silica gel column was used. The oven temperature was 23° and the flow rate 175 cc min^{-1} . The eluted carrier gas was bubbled directly into aqueous NaOH containing a known quantity of Na_2CO_3 .

iii. Amines.

An eight-foot glass column that contained 20% glycerol on base-washed firebrick was used. The oven temperature was 95° and the flow rate 100 cc min⁻¹.

iv. Hydrogen Cyanide.

An eight-foot glass column of 20% di-(2-ethylhexyl)-sebacate on celite was used. The oven temperature was 23° and the flow rate 100 cc min⁻¹.

Elution times for carrier-free compounds were pre-determined by use of macroscopic injections of their nonradioactive counterparts.

(c) Aqueous Dissolution of Target.

A target sample was dissolved in weakly alkaline solution (ca. 0.1 M NaOH) that contained one or more carriers (0.1 M). The carriers were isolated, then converted to BaCO₃.

i. Non-Acidic Gases.

The solution containing the target was degassed by sweeping with CO₂-free air. The released gases were swept over copper oxide at 800°, trapped in aqueous NaOH containing a known amount of Na₂CO₃, then collected as BaCO₃.

ii. Hydrogen Cyanide, Hydrolyzable, Cyanamide, and Guanidine.

The procedures used were those described above in Sections B. 2(d) and B. 2(g).

(d) Separation by Recrystallization.

i. Tetrazole and Polymer.

A small sample of irradiated tetrazole together with a larger sample of carrier tetrazole were dissolved in hot ethyl acetate. The solution was filtered to remove the dark brown residue. The residue was washed with cold ethyl acetate, then dissolved in hot 0.5 M NaOH. KMnO_4 was added to this alkaline solution, which was refluxed for two hours. The resulting CO_2 was collected as BaCO_3 , which was designated as Polymer. The filtrate was reheated to dissolve the tetrazole. Since the solution remained slightly colored, decolorizing carbon was added to remove polymeric residues and soluble labeled products that could otherwise be adsorbed on recrystallizing tetrazole. The solution was again filtered, and the solution boiled down to facilitate recrystallization. The tetrazole crystals obtained were recrystallized yet again from ethyl acetate, then oven dried before combustion over hot CuO to CO_2 and finally BaCO_3 .

ii. 1,2,4-Triazole.

A mixture of a small sample of irradiated tetrazole and a larger amount of 1,2,4-triazole carrier was dissolved in hot 5/1 benzene-ethyl acetate. The solution was filtered to remove the brown residue, then decolorized with carbon to removed additional polymeric residues and possible adsorbable impurities. The hot solution was filtered again, boiled down, then allowed

to cool. The 1,2,4-triazole obtained was then recrystallized before being converted to BaCO_3 .

(e) s-Tetrazine.

The s-tetrazine carrier was prepared from s-tetrazine-3,6-dicarboxylic acid after the procedure of Wood and Bergstrom;³⁰ the product was purified by sublimation under water aspirator vacuum at 70° . Samples of carrier and target were intimately mixed, transferred to a glass sublimer, then heated to 70° under aspirator vacuum. After the carrier had collected onto a cold finger, the sublimer was heated to 200° to release labeled s-tetrazine from the target. The separated s-tetrazine was next purified by resubliming at 70° under aspirator vacuum. It was combusted over copper oxide at 800° , then converted to BaCO_3 .

(f) Radioactivity Determinations.

The procedures employed are those described in Section B. 2(1).

(g) Total Target Specific Activity.

Two methods were used, permanganate combustion, as described in Section B. 2(m), and combustion over copper oxide at 800° . In the latter procedure, a weighed sample of target in a porcelain boat was heated to 800° in a tube furnace. A stream of CO_2 -free air passed over the boat, through a copper oxide bed at 800° , and on through an aqueous sodium hydroxide trap. The trapped carbonate was collected as BaCO_3 .

3. Results.

(a) Total Specific Activity of Irradiated Tetrazole Specimens.

Table VII gives the results of determinations of total activity per gram of two specimens of tetrazole, irradiated in different positions in the Reactor.

Table VII
~~Table VII~~

Total Specific Activity of n-Irradiated Tetrazole Specimens

Method	Counts per Minute per Gram of Target	
	Specimen 1	Specimen 2
KMnO ₄ Combustion	1.54×10^6	---
Combustion over CuO	1.38×10^6	1.81×10^6
Combustion over CuO	1.44×10^6	1.89×10^6
Average	$(1.45 \pm 0.06) \times 10^6$	$(1.85 \pm 0.04) \times 10^6$

(b) Distribution of C¹⁴ Activity.

The values obtained from gas chromatographic and chemical separations are given in Tables VIII and IX, respectively. The large yield of Polymer is consistent with that found in related targets.³¹ For example, Polymer accounted for 59% of the total C¹¹ activity found in cyclopentadiene.²⁸

Table VIII

 C^{14} -Labeled Products: Gas Chromatographic Separations

<u>Fraction^a</u>	<u>Total Activity (%)</u>
Total Volatile	3.9 $\pm$ 0.9
$C^{14}O_2$	1.6 ^b
$HC^{14}N$	1.0 $\pm$ 0.1
Amines ^c	0.0 $\pm$ 0.0

^a Specimen 1^b One determination; others are duplicate determinations.^c CH_3NH_2 , $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(CH_3)_3N$.

Table IX

 C^{14} -Labeled Products: Chemical Separations

<u>Fraction</u>	<u>Total Activity (%)</u>
Tetrazole	2.6 $\pm$ 0.7 ^{a,c}
1,2,4-Triazole	1.4 $\pm$ 0.1 ^{a,d}
s-Tetrazine	2.2 $\pm$ 0.1 ^{a,d}
$NH_2C^{14}N$	5.8 $\pm$ 0.8 ^{a,d}
$C^{14}NH(NH_2)_2$	3.6 $\pm$ 0.1 ^{a,b,d}
$HC^{14}N$	2.4 ^{b,e}
Hydrolyzable	3.8 ^{b,e}
Non-Acidic Gases	0.3 ^{b,e}
<u>Polymer</u>	<u>53.8 $\pm$ 0.6 ^{a,d}</u>
Total Recovered:	76

^a Specimen 1^b Specimen 2^c Triplicate runs^d Duplicate runs^e Single run

4. Discussion.

As in alkali azides, one would expect high hot zone temperatures for very short time intervals in tetrazole. Accordingly, the recoil C^{14} atom in the hot zone could react with highly excited tetrazole molecules or pieces of tetrazole molecules fragmented because of the high temperature. Again, like the alkali azides, the rapid cooling of the hot zone would quench these reactions short of completion, leaving the hot atom in the form of reactive intermediates or precursors. These precursors would remain entrapped in the crystal structure until released by the initiation of separation procedures. Therefore, the final distribution of labeled products depends not only upon the nature of the precursors but also upon the means by which the precursors are released and the nature of their surroundings at the time of release.

(a) Tetrazole, 1,2,4-Triazole, and s-Tetrazine.

Kaplan and Wilzbach³² produced benzvalene (II) by

II

III

photolyzing benzene, and Lahmani and Ivanoff³³ proposed a diazabenzvalene intermediate (III) to account for photolytic products of pyrazines. The existence of II and the supposed existence of III suggests that tetrazabenzvalenes could be intermediates formed

in irradiated tetrazole. Three such intermediates are possible, resulting from electrophilic attack upon tetrazole by atomic carbon, thus:

s-Tetrazine, 1,2,4-triazole, and guanidine could result from intermediate IV according to the following scheme:

Additional hydrogen, as required for example to form guanidine from its skeletal intermediate, would be extracted from the solvent. In the above scheme, lone pairs of electrons on nitrogen are omitted.

Tetrazole could result from VI, as follows:

as-Tetrazine could be formed in principle from IV and V, as could v-tetrazine from V and VI. However, neither as- nor v-tetrazine are known to exist,³⁴ so their decomposition fragments, C¹⁴N radical and NC¹⁴-CN radical, respectively, would be expected instead.

Other reactive intermediates can be proposed that will account for s-tetrazine, 1,2,4-triazole, tetrazole, and guanidine, such as the various possible bicyclic intermediates and intermediates formed from insertion of C¹⁴ into C=C, C=N, N=N, and C-H bonds.^{28,29,35} However, we have proposed tetrazabenzvalene intermediates because the hydrocarbon analogue, benzvalence, is known to exist.³² The yield of labeled products in γ -irradiated cyclopentadiene²⁸ can be interpreted in terms of the benzvalene intermediate. Indeed, two products, fulvene and benzene, were observed by Kaplan and Wilzbach from the collapse of the intermediate.³²

Labeled hydrogen cyanide and cyanamide could result from different fragmentations of the tetrazabenzvalene intermediates. Since the intermediates would be entrapped in the crystal lattice

structure under strain, sufficient activation could be present to facilitate the required bond ruptures upon dissolution of the target in solvent. Alternatively, HC^{14}N and $\text{C}^{14}\text{NNH}_2$ could be products of the reaction of the recoil atom with various fragments of tetrazole thermally decomposed in the hot zone. The labeled C^{14}O_2 indicates scavenging of the hot atoms by trace air oxygen, moisture, or recrystallizing solvent. The Hydrolyzable fraction includes this C^{14}O_2 and probably includes as well carbonate resulting from hydrolysis of some of the cyanamide activity.

The polymeric material in the irradiated tetrazole specimens must arise in part from radiation damage. Approximately 10% by weight of the target specimens was this residue. Labeled tarry residue could result from the reaction of labeled intermediates (such as the tetrazabenzalenes) with various fragmentation products in the hot zone as well as with subsequent radiation induced fragments of tetrazole.

II. KINETICS OF DEUTERATION OF FIVE-MEMBER AROMATIC HETEROCYCLES

A. Introduction.

In recent years, considerable attention has been focused upon the relative electrophilic reactivities of various ring sites in aromatic heterocyclic compounds.³⁶⁻⁴⁵ The electrophilic reactivities depend upon the nature of the substrate and the nature of the electrophile. Theoretical interpretations of the relative reactivities of ring sites have been hindered by the dearth of rate studies upon these systems. In order that different positions of a given substrate be compared for the same or different electrophilic reagents, it is important that the kinetics of substitution for each site and each reaction be known. From the observed rate laws, one may formulate mechanisms, which in turn serve as guides in comparisons of reactivity. For example, kinetic data may often indicate the form of the substrate (i.e., whether the free molecule or its conjugate acid or base) and the form of the electrophile involved in a given reaction.³⁸

Hydrogen isotopic exchange reactions are particularly useful for reactivity comparisons for the following reasons: (1) It is possible to study essentially all sites in substrates so that a very large spectrum of reactivities of sites in various molecules may be obtained. (2) Isotope effects, if present, are large. (3) The substituting group and the leaving group are isotopes, so that models of the transition state that include the electrophile

are comparatively simple. This report describes studies of the kinetics of deuteration of pyrazole (I), imidazole (II), and 1,2,4-triazole (III).

B. Pyrazole and Imidazole.

The investigations on these two substrates is described in detail in the following two manuscripts:

1. E. C. Wu and J. D. Vaughan, "The Kinetics of Deuteration of Pyrazole," J. Org. Chem., 35, 1146 (1970).
2. J. D. Vaughan, Z. Mughrabi, and E. C. Wu, "The Kinetics of Deuteration of Imidazole," ibid., 35, 1141 (1970).

Reprints of these manuscripts are attached.

C. 1,2,4-Triazole.

1. Experimental.

Materials. 1,2,4-Triazole from Aldrich Chemical Company was recrystallized three times from a benzene-ethanol solution (4:1 by volume), mp 120°. The NMR spectrum of 1,2,4-triazole exhibited two singlets ($\delta = 4.8$ and $\delta = 8.5$) attributed to

hydroxyl protons and protons in equivalent 3 and 5 positions, respectively. In both substrates, it is clear that nitrogen protons exchange rapidly with deuterons in heavy aqueous solution.

Kinetic Runs. The details of the kinetic procedures are given elsewhere.⁴⁶ The ionic strength of solutions was adjusted to 1.0 M by measured addition of heavy aqueous NaCl. All deuterations were carried out in 100 ml round bottom flasks held at constant temperature in a water bath. Aliquots of 2 ml each were removed periodically, then thermally quenched (0°). Proton peak areas for substrate exchange sites were determined for each aliquot using the Varian A-60A spectrometer.⁷ Pseudo-first order rate constants ($k_1^{\text{obsd.}} = k_2[\text{D}_2\text{O}]$) were obtained from (-slope of $\ln(\text{Peak Area})$ vs. time plots.

pD values were measured at room temperature with the Beckman Zeromatic pH meter, corrected by the formula of Glaskoe and Long ($\text{pD} = \text{meter reading} + 0.4$).¹⁴ The pK_a value for 1,2,4-triazolium cation was determined in heavy water solutions at ionic strength of 1.0 M and at buffer ratios $[\text{Triazole}]/[\text{Triazolium}]$ of 1/1 and 1/3. The value $\text{pK}_a = 2.8 \pm 0.1$ is the average of two measurements.

Temperatures were reproducible to within $\pm 0.1^\circ$ and rate constants to within $\pm 10\%$. Uncertainties in concentrations arising from thermal changes in volume are discussed elsewhere.⁴⁶

2. Results.

(a) Deuteration of 1,2,4-Triazole.

Rates of deuteration of the 3(5) position in 1,2,4-triazole were measured as functions of pD ,* ammonia buffer concentration, and temperature. The effect of pD upon the pseudo-first order rate constant ($65^{\circ}C$) is illustrated in Figure 2; pD rate profiles similar in appearance to this one have been observed for 1-methylimidazole,³⁹ imidazole,⁴⁶ and thiazole⁴⁴ In these rate profiles, the rate constant drops abruptly with decreasing pD in the region of substrate self-buffering. Thus, at $pD = pK_a = 2.8$, $k_1^{obsd.}$ for 1,2,4-triazole is half that at $pD > 5$. In ammonia buffered runs, the buffer ratio $[NH_3]/[NH_4^+]$ was fixed at 3.2 ($pD = 10.4$). In seven runs, with NH_3 ranging from 0.010 M to 1.73 M , the value of $k_1^{obsd.}$ remained constant at $9.6 \times 10^{-5} \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$, indicating no ammonia buffer catalysis.

Activation parameters were determined from runs made at 65° , 70° , and 75° ; $k_1^{obsd.}$ values were $3.1 \times 10^{-5} \text{ sec}^{-1}$, $9.8 \times 10^{-1} \text{ sec}^{-1}$, and $23.7 \times 10^{-5} \text{ sec}^{-1}$, respectively. The experimental activation energy obtained from these results is $23 \pm 2 \text{ Kcal}$ and the $\log A$ value is 13 ± 1 .

3. Discussion.

Mechanism: 1,2,4-Triazole. The pD rate profile exhibited in Figure 2 is consistent with the conjugate acid of 1,2,4-triazole

* Measured at room temperature.

FIGURE 2: DEPENDENCE OF THE RATE OF DEUTERATION
OF 1,2,4-TRIAZOLE UPON PD AT 65°.

being the substrate. Two tautomers of this conjugate acid are possible:

Operationally, one cannot distinguish V and VI in aqueous solution, nor discriminate between exchange sites 3 and 5, because of the rapid hydrogen exchange that occurs at nitrogen atoms 1, 2, and 4. However, one can predict that the most labile carbon-bonded proton in either tautomer would be that in the 5 position in VI.⁴¹ Thus the ylide intermediate (VII) would be particularly stabilized by

the formally positive >NH groups in positions 1 and 4. Utilizing VI and VII, one obtains the following scheme:

Subsequent deuteration of the remaining carbon site (3) could occur by the same sequence after rapid deuterium transfer from position 1 to position 2. In this application of scheme 1, it has been shown^{44 45} that

$$k_1^{\text{obsd.}} = k_b K_w / (K_a + [D^+]) \quad (1)$$

where $K_w = [D^+][OD^-] = 2.9 \times 10^{-15}$ and $K_a = 1.6 \times 10^{-3}$ (see Experimental). An excellent fit of the data is obtained if k_b is set equal to $8 \times 10^7 \text{ sec}^{-1} \text{ l. mol}^{-1}$ (solid line in Figure 2).

If $[D^+] \ll K_a$, eq 1 reduces to

$$k_1^{\text{obsd.}} = k_b \frac{K_w}{K_a} \quad (2)$$

Eq 2 is applicable for $\text{pD} \gtrsim 5$.

(b) Relative Rates of Deuteration.

Most of the rate data on hydrogen exchange in five-member heterocyclic cations reported in the literature^{41,43-45} were taken at 31° and 33°. Comparison of our results for 1,2,4-triazolium cation with the reported data requires reduction of $k_{\text{obsd.}}$ from 65° to 33°, then calculation of the second order rate constant k_b from eq 2. The k_b value for 1,2,4-triazolium cation at 33° was determined in this way to be $1.5 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$. The following order for hydrogen exchange in cations is obtained:

The rates of deuteration of the 4(5) position in imidazolium cation⁴⁶ and the 3(5) position in pyrazolium⁴⁷ were measured at 180° and 230°, respectively. If the $k_1^{\text{obsd.}}$ value for 3(5) deuteration of pyrazolium is reduced from 230° to 180°, the ratio of k_p values for the two substrates can be roughly estimated by the expression $(k_1^{\text{obsd.}})(K_a, \text{Im}) / (k_1^{\text{obsd.}})(K_a, \text{Py})$ to be 10^{-2} . Here, K_a for imidazolium and pyrazolium cations are room temperature values.³⁴ From this result, the following additional order of cationic hydrogen exchange reactivities is suggested: 1,2,4-triazolium (3(5) position) > imidazolium (2 position) > pyrazolium (3(5) position) > imidazolium (4(5) position). As expected,² the exchange reactivity of 1,2,4-triazolium cation lies between that of 1,4-diethyltetrazolium cation⁴¹ and the imidazolium cation.⁴⁶

In discussing the relative reactivities of cationic substrates undergoing hydrogen exchange, the ylide intermediate is probably a reasonable model for the transition state.^{41,43,46} That is, factors that stabilize the ylide intermediate would also tend to stabilize the transition state leading to the intermediate. If a β carbon atom in imidazolium cation is replaced by a nitrogen heteroatom to yield 1,2,4-triazolium, the rate constant is enhanced by a factor of 10^3 ; this enhancement is comparable to that observed by Olofson *et al*⁴⁵ when an extra nitrogen was added to thiazolium salts. A second β nitrogen added to imidazolium, to yield tetrazolium, produces an additional rate constant increase of 10^{11} . It is evident

that the second extra nitrogen heteroatom provides a much greater stabilization in the ylide intermediate than did the first heteroatom. Further, it appears that a vicinal pair of nitrogen heteroatoms (as in 1,2,4-triazolium) stabilizes the five-member ylide to the same extent as a single sulfur heteroatom (as in thiazolium).

In a preceding paper,⁴⁶ it was suggested that CNDO/2 ylide and anion stabilization energies [$\Delta E_T = E_T(\text{intermediate}) - E_T(\text{substrate})$] can be useful indices for base catalyzed exchange reactivity in heterocycles. Here E_T is the valence electronic energy plus the core repulsion energy. Thus, ΔE_T value correctly indicated the most reactive positions in various five-member heterocycles, correctly ordered the exchange reactivities of five of six cationic substrates, and correctly indicated that cationic substrates are considerably more reactive than the corresponding neutral molecular substrates (e. g., imidazolium vs. imidazole). ΔE_T values were calculated for 1,2,4-triazolium and tetrazolium cations by the same calculational procedure and geometries employed before; the results are given in Table X, together with comparative results for imidazolium⁴⁶ and 4-methyloxazolium.⁴⁶ The predicted reactivity order is, therefore, 4-methyloxazolium > tetrazolium > imidazolium > 1,2,4-triazolium, which does not agree well with the observed order tetrazolium > 4-methyloxazolium > 1,2,4-triazolium > imidazolium. In view of these results, it would

appear that the good agreement between calculated and observed reactivities of heterocycles with two heteroatoms does not extend to heterocycles with more than two heteroatoms.

Table X
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CNDO/2 Ylide Stabilization Energies (Atomic Units)

Imidazolium (2-position)	0.63
4-Methyloxazolium (2-position)	0.60
1,2,4-Triazolium (3(5)-position)	0.65
Tetrazolium	0.61

III. PERSONNEL

In addition to the principal investigator, the following personnel contributed to the investigations described in this report:

- (1) R. L. Springborn, Hot Atom Chemistry (KN_3)
- (2) W. A. Smith, Hot Atom Chemistry (KN_3)
- (3) V. L. Vaughan, Hot Atom Chemistry (KN_3 , NaN_3)
- (4) W. A. Mans, Hot Atom Chemistry (NaN_3)
- (5) B. Michrina, Hot Atom Chemistry (Tetrazole)
- (6) Z. Mughrabi, Hydrogen Isotopic Exchange (Imidazole)
- (7) E. C. Wu, Hydrogen Isotopic Exchange (Pyrazole,
Imidazole, 1,2,4-Triazole)

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