col was produced and isolated in nearly theoretical current yield. This actual demonstration of a reduction occurring in the anode compartment of an electrolytic cell and its quantitative correlation with a lowering in the V_i value for magnesium lends credence to the postulate that an observed lowering in the V_i value for any of the active metal anodes considered in these studies always indicates that reduction of some species in the anolyte has taken place. In short, the V_i value has true chemical significance and represents a convenient measure of the extent of anodic reduction.

The Anodic Behavior of Indium and Thallium.—Except for the recent preparation of aluminum(I) iodide,[6] the chemistry of the active metals whose anodic behavior has just been discussed is characterized by a notable lack of solid compounds in which the elements exhibit any oxidation state other than that corresponding to their number of valence electrons. In contrast to this, indium and thallium form well-defined compounds containing these metals in lower valence states. Thus for indium, mono- and dihalides have long been known, and compounds of unipositive thallium are generally more stable than those of the tripositive element.

The behavior of indium and thallium as anodes in pyridine solutions is consistent with the relative stability of lower oxidation states of these elements. When indium was oxidized anodically in pyridine containing lithium chloride *alone* as electrolyte, a V_i value of 2.41 ± 0.17 (for five experiments) was obtained, and a residue of metallic indium invariably formed in the anolyte. The metal is considered to result from a disproportionation of a lower valent indium species.

$$3In^+ = 2In + In^{+++}$$

A similar disproportionation has been reported for lower valent indium in aqueous, acetic acid[2] and liquid ammonia solutions.[7] The electrolytic oxidation of a thallium anode in lithium chloride–pyridine solutions gave a V_i value of 1.05 ± 0.07 (for five experiments). Neither the indium nor the thallium electrode was attacked non-electrolytically by the lithium chloride–pyridine solution, but there was some loss in weight of the thallium cathode during electrolysis. In view of the low V_i values obtained for these metals in the presence of a non-oxidizing inorganic electrolyte, no experiments with organic potential electron-acceptors were performed.

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for a research grant which made this investigation possible.

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[6] W. C. Schumb and H. H. Rogers, THIS JOURNAL, **73**, 5806 (1951).

[7] A. D. McElroy, J. Kleinberg and A. W. Davidson, *ibid.*, **74**, 736 (1952).

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Carbon Compounds Produced by Pile Neutron Irradiation of Crystalline Ammonium Sulfate: Target Dissolved in Water

BY PETER E. YANKWICH AND W. R. CORMAN, JR.

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The radiocarbon activities produced when pile neutron-irradiated ammonium sulfate crystals are dissolved in water or 1 *M* sodium hydroxide have been subjected to chemical fractionation. Carbon dioxide is formed in greatest amount (40% of the total activity); other radio compounds formed are methylamine (16%), formic acid (16%), formaldehyde (13%), urea (7%), cyanide (6%), and carbon monoxide, methanol and methane (each less than 3%). Comparison of these yields with those obtained from irradiated ammonium bromide demonstrates clearly the role of oxygen in the crystals as a scavenger for highly reduced combinations including the nascent carbon, but does not permit a clear decision in any particular case as to whether or not the radio compound is formed as such in the sulfate crystals.

When samples of neutron-irradiated ammonium bromide are dissolved in water, numerous one-carbon compounds containing C^{14} can be identified among the products. Of the total radiocarbon in such a sample, about 11% is in the form of oxygen-containing compounds (carbon monoxide and dioxide, formic acid, formaldehyde, methanol, and urea), while the remainder consists of small amounts of methane and cyanide and a very large amount of methylamine.[1] While some of the oxygen-combined activity may be due to reactions of nascent carbon with water, air or other impurities in the crystals irradiated, it may be due also to combination with the solvent water of carbon-containing groups of atoms trapped under strain in the irradiated solid. In an effort to learn more concerning the fate of the recoil carbon in the nuclear reaction $N^{14}(n,p)C^{14}$, we have subjected a sample of ammonium sulfate to pile-neutron irradiation and have performed chemical fractionations of the radiocarbon compounds which result when samples of this target material are dissolved in water and in 1 *M* sodium hydroxide.

Experimental

Sample Preparation and Irradiation.—Twenty grams of reagent grade ammonium sulfate was dried at 110° for two hours then placed in a quartz tube which was stoppered with a perforated cork (to permit escape of hydrogen or other gaseous evolute during the course of the irradiation), and the whole enveloped in Parafilm to exclude air. (The crystals occupied about two-thirds of the tube volume. A stream of dry helium was used to displace included air before the tube was sealed.) The pile irradiation was carried out at the Argonne National Laboratory, whose staff kindly recorded the following: irradiation time, 1172 hours; sample temperature, 36°; X-ray and γ-ray flux, 530 R. min.$^{-1}$; neutron flux, approximately 10^{12} cm.$^{-2}$ sec.$^{-1}$. The sample was allowed to cool off for six months following

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[1] P. E. Yankwich and J. D. Vaughan, THIS JOURNAL, in press.

irradiation, then transferred to an ordinary weighing bottle from which small samples were withdrawn for analysis. The irradiated crystals were in contact with air for the 9 months during which the analyses were performed. No significant changes were noted in either the total activity per unit weight of sample or the distribution of radiocarbon over various chemical forms during this period; this observation is to be contrasted with that recorded for the ammonium bromide sample,[1] where such changes were found.

Chemical Fractionation Procedures.—The carriers employed in this study were: carbon dioxide, carbon monoxide, methane, cyanide, methylamine, formic acid, formaldehyde, methanol, urea and guanidine. The gases were separated by differential absorption and combustion; the non-gaseous carriers were isolated either by distillation procedures, by derivative preparation, or by specific chemical reaction. The techniques have been described in detail elsewhere.[1] The results are collected in Table I; the last column is the approximate distribution of activity found for ammonium bromide.

A number of the results require annotation.

Carbon Dioxide and Cyanide.—When cyanide carrier is present the analysis often is complicated by occurrence of the cyanohydrin reaction with formaldehyde. Once the level of the cyanide activity had been established, potassium cyanide was usually left out of the carrier solutions which were added to the water solution of the target material. In such cases it was observed that the apparent activity of the carbon dioxide fraction was higher than when the cyanide was present in macroscopic amount. It is likely that this result is due to oxidation by the carriers added, formic acid, formaldehyde, etc., or air in the sweep gas, of the trace cyanide to carbon dioxide, possibly through the intermediate stage of cyanic acid. An alternative calculation for the percentage cyanide activity can be made by taking the difference of the two averages for carbon dioxide fraction activity. **Carbon Monoxide and Methane.**—A similar calculation can be made for carbon monoxide, since in a number of experiments no attempt was made to separate carbon monoxide and methane activities. **Methylamine.**—This fraction might better be labeled *total basic*, since all of the values shown were obtained by distillation fractionation of non-gaseous carrier activities. One result, 18.3%, was obtained by extraction of methylamine into chloroform and preparation of the hydrochloride; also in a single experiment, guanidine, isolated as the picrate, was found to be inactive. These two pieces of information suggest that no other basic substance is present in the fraction in appreciable quantity. **Formaldehyde.**—All results shown were obtained by analysis of the methone derivative; the distillation separation values were not significantly different. **Formic Acid.**—All the values given in the table were obtained by measurement of the radioactivity of carbon dioxide produced from the reaction of mercuric acetate with degassed target solution. The average of results obtained by the distillation procedure is the same as that shown in the table, but the mean deviation was somewhat larger.

TABLE I

RADIOCARBON DISTRIBUTION: $(NH_4)_2SO_4$ TARGET, H_2O SOLVENT

Fraction	% of total activity Average	Values obtd.	Obsd. for NH_4Br
CO_2	39.5 ± 0.3	38.9, 39.4, 39.8, 39.7	1.7
CO	2.0 ± 0.4	1.8, 1.7, 2.6	1.3
CH_4	0.5 ± 0.1	0.6, 0.5, 0.4, 0.5	7.5
HCN	3.9 ± 0.3	3.5, 3.9, 4.2	2.0
CH_3NH_2	16.1 ± 1.2	14.2, 14.5, 17.8, 15.8, 16.0, 14.5, 17.5, 18.4, 16.0	79
HCOOH	15.5 ± 0.5	15.9, 16.0, 14.5, 15.8, 15.4	1.3
HCHO	13.2 ± 0.2	13.2, 13.2, 13.0, 13.0, 13.5, 13.7, 13.2	5.8
CH_3OH	0.7 ± 0.1	0.7, 0.6, 0.8	0.4
$CO(NH_2)_2$	7.3 ± 0.5	8.4, 7.2, 7.2, 5.9, 7.3, 7.7	0.4
$CNH(NH_2)_2$	$0._0 \pm 0._4$	$0._0$	0.0
CO_2 + HCN	45.0 ± 1.0	43.9, 46.8, 44.0, 44.6, 45.5	
CO + CH_4	2.7 ± 0.3	2.8, 3.5, 2.5, 2.6, 2.8, 2.1	
HCN (calcd.)	(5.5 ± 1.0)		
CO (calcd.)	(2.2 ± 0.3)		

The sum of the percentage activities of the individually isolated carrier fractions is 98.8 ± 1.5. If the calculated carbon monoxide and cyanide data, obtained from the results of combined carrier analyses, are employed, the sum is 100.6 ± 1.8%.

Two experiments were performed in which the weighed sample of ammonium sulfate was dissolved in 1 *M* sodium hydroxide rather than freshly distilled water; urea and methane fractions were lost by accident. For the other radioactivities, amounting to over 90% of the total, *no difference* in distribution was noted.

Discussion

In an earlier study[2] it was found that most of the activity produced in irradiated beryllium nitride appeared as methane when that material was dissolved in dilute alkali. Apparently, much of the C^{14} in the crystals was in essentially carbide form, and reaction with water occurred upon solution of the target substance. In the case of ammonium sulfate it is possible that many of the radiocarbon compounds found in the solution of irradiated sample were produced *as such* in the crystalline matrix. It is also possible that these same activities result from reactions with the solvent of carbon-containing species trapped under strain in the solid.

Carbon monoxide may be mentioned as a case in point. The data summarized in Table I show that the large amount of carbon dioxide activity found in ammonium sulfate is accompanied by only a small amount of carbon monoxide. In studies on saturated ammonium nitrate solution, where both hydrogen and oxygen are abundant, as in the ammonium sulfate, previous workers have found comparable amounts of the two oxides.[3,4] Carbon monoxide may be present in ammonium sulfate in such a state that its hydration to formic acid upon solution of the target is favored. Phase effects of a related type have been observed in several situations by Libby and his co-workers.[5] On the other hand, the low abundance of carbon monoxide in ammonium sulfate may be related directly to the formation of large amounts of other oxygen-containing species; reaction of a nascent C–O combination with H and O to produce the skeletons of more complicated molecules may be favored.

The yields of methane, methylamine, formic acid and formaldehyde in the bromide and sulfate reflect in simple manner the presence or absence of oxygen in the target compound; but whether or not the latter two are produced as such in the irradiated sulfate cannot be determined from the limited amount of information available. For example, formic acid may be formed from a trapped CO as described above, from a lattice-stabilized COOH radical which abstracts hydrogen from the solvent, etc. In the presence of sulfate oxygen nascent methylamine or its precursor might be converted in part to an imine, $CH_2{=}NH$, before achieving equilibrium in the crystal matrix; this imine would be hydrolyzed to formaldehyde when the crystals were dissolved. (The observed independence of the radiocarbon distribution on *p*H of the solvent suggests that whatever reactions occur upon solution of the target are primarily with water substance, but

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[2] P. E. Yankwich, *J. Chem. Phys.*, **15**, 374 (1947).

[3] P. E. Yankwich, G. K. Rollefson and T. H. Norris, *ibid.*, **14**, 131 (1946).

[4] L. Norris and A. Snell, *Nucleonics*, **5**, [3] 18 (1948).

[5] Libby and co-workers, *J. Chem. Phys.*, **17**, 647 (1949); **20**, 487 (1952); **21**, 1495 (1953).

furnishes no clue as to the relative importance of these reactions to *in situ* build-up in the formation of the various radiocompounds which were found.)

Methanol presents a problem like that of carbon monoxide; the yields of both are essentially similar from the bromide and the sulfate targets. This may be an indication that methanol is formed from an oxygen free precursor, such as CH_2, in both crystals, though this is highly unlikely in view of the comparative yields of formic acid, etc. In the case of the sulfate target there is the possibility for protomethanolic precursors to be scavenged efficiently by oxygen to yield eventually less highly reduced activities; this would account for the low methanol yield from that target material.

A related situation seems to be reflected in the yields of urea and guanidine. In the presence of sulfate oxygen the amount of urea formed is increased, yet no appreciable quantity of guanidine was produced in the bromide case. In the sulfate lattice the N–CO–N skeleton, more or less embellished with hydrogen, apparently is more stable with respect to simpler combinations than is the N–CN–N skeleton in the ammonium bromide. Alternatively, the N–C–N part of the urea–guanidine skeleton may be effectively broken up in the halide matrix by hydrogen to yield methylamine or its precursors, while guanidine or protoguanidine formed in the sulfate may be hydrolyzed virtually completely to urea upon solution of the target. Considerable light undoubtedly would be shed upon situations of this type by experiments involving other solvents than water.

Effect of Pile Radiations.—In the foregoing discussion we have presumed that there is no sensible integrated effect of the pile flux of γ- and X-rays. A modest dependence of the retention of bromine in irradiated potassium bromate upon irradiation time has been observed,[6] and such effects may be of importance in the irradiation of ammonium sulfate. In the present situation the picture is complicated not only by the complexity of the apparent radiocarbon distribution, but also by the fact that we have no accurate information concerning the specific origins of any one compound, and so no way of determining from the data recorded above which or what part of any one might have resulted from radiation-induced reactions.

A simple calculation based on radiation dose, the terminal electron fraction of C^{14} in the target, and the assumption that g is 30 e.v. per ion pair, indicates that the chance for direct influence of radiation on the state of radiocarbon at the end of the irradiation is of the order of 0.001. This is an approximate lower limit for the occurrence of a radiation effect.

Gamma or X-ray induced events near a carbon should be expected to affect the final chemical state of that carbon; one must, however, decide what is meant by *near*. If we assume arbitrarily that a radiation-induced event occurring within a volume, about a carbon, containing 25 sulfate ions and 50 ammonium ions affects the final chemical state of the carbon, the chance that such influence occurs is roughly 0.3. This is an approximate upper limit for the occurrence of a radiation effect.

It seems likely that the steady state concentration of reactive species produced by the pile radiation flux is sufficiently large to be capable of exerting only secondary influence.

Acknowledgments.—We wish to express our thanks to Dr. J. D. Vaughan, who performed some of the preliminary experiments on this target material. This research was sponsored by the A. E. C.

[6] G. E. Boyd, J. W. Cobble and Sol Wexler, THIS JOURNAL, **74**, 238 (1952).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

Isotopic Exchange Reactions of Phosphorus Pentachloride[1]

BY JAMES J. DOWNS[2] AND ROWLAND E. JOHNSON

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The rate of exchange between phosphorus pentachloride and labeled chlorine in solvent carbon tetrachloride shows a difference in reactivity for the various chlorine atoms in the pentachloride molecule, three chlorine atoms reacting rapidly and two slowly. Chlorine, on addition to phosphorus trichloride, enters mainly into the equatorial positions; mercury attacking phosphorus pentachloride removes chlorine mainly from the equatorial positions. Mechanisms are proposed and an explanation for the difference in reactivities is suggested. In addition, the isotopic exchange reactions in carbon tetrachloride between chlorine and phosphorus oxychloride and between phosphorus trichloride-Cl^{36} and phosphorus pentachloride have been found to be measurably slow.

Introduction

In general, those compounds in which the central atom has a coördination number of five are quite unstable and not numerous,[3] so that information regarding their chemical characteristics and structural properties is relatively scarce and uncertain. Consequently, theoretical considerations of bond hybridization[4,5] are conjectural and unsatisfactory. Attempts to show a non-equivalence of atoms in such molecules as phosphorus pentachloride and phosphorus pentabromide by the use of isotopic

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[1] Work performed on Contract No. AT-(40-1)-1317 with the Atomic Energy Commission.

[2] Abstracted from a dissertation presented by J. J. Downs for the degree of Doctor of Philosophy, August, 1954. Complete dissertation on file in Library, Florida State University.

[3] W. Huckel, "Structural Chemistry of Inorganic Compounds," translated by L. H. Long, Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 131.

[4] L. Pauling, "Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1945, p. 92.

[5] R. Daudel, A. Bucher and H. Moureu, *Compt. rend.*, **218**, 917 (1944).