APR 23 1962

BNL 6010

MASTER

LOW-TEMPERATURE STUDIES OF RECOIL REACTIONS*

Slobodanka R. Veljkovic** and Garman Harbottle

Chemistry Department

Brookhaven National Laboratory

Upton, Long Island, New York

Abstract

The Szilard-Chalmers reaction has been investigated in a number of crystalline compounds with a special effort being made to maintain the temperature at low values during bombardment, storage and dissolution. Evidence of rapid thermal annealing at moderate temperatures is found. The data suggest that it will for this reason be extremely difficult to obtain reliable information on the true yields of the hot-atom processes which occurred before any annealing took place.

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

Facsimile Price \$ 2.60

Microfilm Price \$ 1.87

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

* Research performed under the auspices of the U. S. Atomic Energy Commission.

** On leave from the University of Belgrade, Yugoslavia.

LEGAL NOTICE

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

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

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

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

I. INTRODUCTION

In two recent, short communications^(1,2) the authors presented reasons for undertaking the investigation of the Swilard-Chalmers reaction in crystals continuously held at low temperature during the bombardment, storage and dissolution steps. Evidence was presented that annealing reactions were important at, and considerably below, ambient laboratory or reactor temperatures. The influence of thermal annealing, in several cases, was in fact so great as to vitiate entirely any mechanistic interpretations based upon those yields measured at room temperature.

In the present report, more complete data on these systems, and on a variety of others, are presented. The compounds investigated include bromacetic acid, bromacetates, and several oxanion salts. These data confirm, in general, the fear that many retention figures previously reported in the literature actually represent the sum of two quantities: an unknown "intrinsic" retention,⁽³⁾ which could only be measured by an experiment carried out in toto at an indefinitely low temperature, and an unknown increase in retention above this figure due to thermal (and/or radiation) annealing.

II. EXPERIMENTAL

1. Preparation of material for bombardment.

Lithium nitrate was recrystallized twice from water, keeping the temperature above 70°C, to avoid formation of the trihydrate. The anhydrous salt was dried at 120°C and vacuum desiccated over Drierite before use. Potassium permanganate was recrystallized twice from hot water, dried and vacuum desiccated over Drierite. Potassium chromate and dichromate, and ammonium chromate, were the best reagent grade, used without further purification. Sodium chromate tetrahydrate was prepared by recrystallization from aqueous

solutions kept above 30°C , as higher hydrates form below that temperature. Chromium trioxide was recrystallized from water-conc. nitric acid (1:5) solutions, filtered off and vacuum-desiccated over sodium hydroxide pellets: stock-bottle material gave identical results. It was found difficult to recrystallize bromacetic acid, and for this reason, although different lots of crystals gave consistent results, the authors regard these results as possibly subject to systematic error due to impurities. The procedure was to dissolve the bromacetic acid in ether, pass it once through an alumina column and re-evaporate the ether at room temperature, in vacuo. Sodium bromacetate was prepared by neutralizing ethanol solutions of bromacetic acid with ethanolic sodium hydroxide to bromthymol blue end-point, avoiding excess base. The product was recrystallized twice from water and desiccated in vacuo. Potassium bromate was recrystallized from water and desiccated.

All solvents were the purest obtainable grade, and were redistilled before use. It was found imperative to purify the acetone used with permanganate from traces of methanol, and this was done by dissolving potassium permanganate in the acetone in excess, standing (dark) 24 hours, filtering and distilling through a column of 8 to 10 plates. Fresh acetone was prepared every two or three days.

The lithium chloride-water eutectic mixture (designated LiCl in the Tables) has been described.⁽¹⁾

Where irradiated bromacetic acid was dissolved in methanol, an amount of sodium hydroxide calculated to neutralize it was present in the solvent. The same was true when it was dissolved in water. These solvents are designated $\text{MeOH}-\text{OH}^-$ and $\text{H}_2\text{O}-\text{OH}^-$ respectively in the Tables.

2. Bombardments

Thermal neutron irradiations were made in the BNL graphite reactor. The positions were the pneumatic tube (PN 4, flux 4.8×10^{12} n/cm² sec, Cd ratio ca. 100, radiation level ca. 10^7 R/hr) for irradiations at ambient (see below) or dry-ice temperatures. The animal or instrument tunnels (flux about 2.9×10^9 n/cm² sec, Cd ratio ~ 120) were used for irradiations at liquid nitrogen temperature.

Fast neutron irradiations of lithium nitrate to produce the $^{14}\text{N}(n,2n)^{13}\text{N}$ reaction were made at the BNL 60" cyclotron (20 Mev deuterons on beryllium) and of sodium bromacetate to give $^{80}\text{m}\text{Br}$ by $^{81}\text{Br}(n,2n)$ at the Van de Graaff (800 kev deuterons on tritium). Samples were wrapped in cadmium foil to eliminate thermal neutrons.

A few irradiations of potassium permanganate were made in the 3 Gev internal proton beam of the BNL Cosmotron $[^{55}\text{Mn}(p,p3n)^{52}\text{Mn}]$.

All samples were irradiated in the presence of air, in closed ampoules of appropriate materials.

Since the pneumatic tube PN 4 was employed for so many studies, the temperature conditions at the irradiation site were directly measured with a thermocouple. It was found that the temperature rose in the first 15 seconds to $\sim 35^\circ\text{C}$, in one minute to 48°C , 2 minutes to 56°C and from 3.5 minutes onward was about 60°C . It is possible that the temperature of crystal samples in their containers did not rise quite so rapidly as this.

3. Analytical procedures

After irradiation, one portion of the lithium nitrate (for a total-activity determination) was weighed directly into a counting vial and

dissolved. The vial was kept sealed to prevent loss of active gases. Another portion was dissolved in acetone at -60°C and aliquot portions were (a) evaporated to dryness in a stream of nitrogen and (b) treated with sulfamic acid and then evaporated to dryness. The sulfamic acid treatment converted recoil-produced NO_2 or NO_2^- to gaseous form which were then removed. After evaporation, samples (a) and (b) were redissolved and counted. Comparison of the total activity and (a) samples gave the percentage of active gaseous species, while comparison of the total and (b) gave the retention, or percentage of ^{13}N present as nitrate. Positrons from ^{13}N were scintillation counted through their annihilation radiations.

Irradiated potassium permanganate was dissolved in acetone at temperatures from $+21$ to -95°C . The solution was filtered through layers of manganese dioxide on a glass frit. Experimentally it was found that three such filtrations, using fresh layers of aged MnO_2 each time, sufficed to remove all the separable activity. The MnO_2 was then treated with conc. HCl (it was not necessary to dissolve more than the surface layer, which contained all the adsorbed activity), Cl_2 was boiled out of the solution and the activity compared with that of the filtrate by scintillation counting of the ^{56}Mn (2.58 hr). All vessels were checked for ^{56}Mn adsorption on the walls.

Irradiated chromates dissolved in $\text{LiCl-H}_2\text{O}$ eutectic mixture were analyzed by a modification of the lead chromate procedure previously used.⁽⁴⁾ Ten-milliliter aliquot portions of the LiCl-chromate solution (which had warmed up to about 0°C) were withdrawn: one was diluted to about 120 ml with water containing carrier CrIII and CrVI (inactive) and a pH of 2.5 to

3.5. Lead chromate was precipitated, filtered off and washed, yielding the CrVI fraction of the sample. The second aliquot was diluted with 10 ml of water, made basic with NaOH and oxidised with Na_2O_2 , excess peroxide being destroyed on the steam bath. The resultant solution was diluted to 120 ml and precipitated as before, yielding the total chromium fraction. The lead chromate precipitates were dissolved in nitric acid and the ^{51}Cr (27 day) scintillation counted, making use of a single channel analyzer with samples of low activity.

Sodium chromate tetrahydrate and chromium trioxide which had been dissolved in acetone after bombardment were treated as above, except that the acetone was evaporated from the total chromium fraction before the NaOH- Na_2O_2 oxidation. The glass walls of various vessels were checked for adsorption of Cr^{51} from acetone solutions: none was found. Irradiated potassium dichromate dissolved in water was analyzed by the usual procedure. (4)

No solvent suitable for low-temperature dissolution of potassium bromate was found; therefore, it was dissolved, after irradiation, in water at ice-temperature and analyzed by the paper-electrophoresis technique previously employed. (5)

Irradiated sodium bromacetate was dissolved in methanol at low temperatures and a 10 microliter portion of the solution directly analyzed for bromacetate and bromide activities by an electrophoresis technique. (5b) The percentage of organic bromide (principally CH_2Br_2) activity was determined by extraction with toluene. (6,7) Where (n,2n) reactions were observed, the ^{80}Br activity was too low for the electrophoresis technique. Here a silver

bromide precipitation was employed⁽⁷⁾: the methanol solutions were much diluted with water to avoid reduction of silver ion. When bromoacetic acid was dissolved in ether direct electrophoresis could not be used because of the apparent exchange of bromine between bromoacetate and bromide. Hence, ether solutions were used only for determination of active CH_2Br_2 , which did not exchange. Bromine-80m activity was determined by either proportional or scintillation counting and ^{82}Br by scintillation counting.

In all radionuclide determinations, appropriate corrections for background, decay, and counting efficiency were applied. Since several of the low-temperature procedures employed novel solvents or reagents, in every case comparisons were made between a standard method for determination of the retention and the low-temperature method, with each applied to the same sample of room-temperature-irradiated and annealed material. For a low-temperature method to be acceptable, it was required that it give a retention for room temperature annealed material close to the conventional value.

III. RESULTS

The experimental results are presented in Tables 1 to 4. Some of these results have been given in our preliminary communications.^(1,2) Unless otherwise noted, figures are averages of at least two, and in some cases as many as eight, determinations. The bombardment temperatures are nominal, liquid nitrogen being indicated by -195°C , dry ice by -78 , ambient (room) by $+25$, which also is applied to bombardments in FN 4 for 10 or 15 seconds (see "Bombardments" above) and 3 minute bombardments in FN 4 by $+30$, nearly the final temperature attained. The "storage" temperature applies from the moment of removal of the sample from the bombardment site and the dissolution

temperature should also be considered as subject to variations of a few degrees. Under the heading "Medium" Acet. = purified acetone, LiCl = LiCl-H₂O eutectic mixture, H₂O = water containing inactive carriers, Ether = redistilled diethyl ether, MeOH = redistilled methanol, MeOH-OH⁻ and H₂O-OH⁻, methanol and water made basic with NaOH, see "Experimental" Section 1.

Errors attached to the results in the Tables are $\pm 0.6\%$ in the chromate series, $\pm 0.3\%$ in the bromates, bromacetates and permanganates, about $\pm 0.8\%$ in bromacetic acid, $\pm 1\%$ in lithium nitrate and $\pm 4\%$ in figures preceded by "ca".

IV. DISCUSSION

Comparison with other authors

If our results are compared with those of other authors, reasonable agreement is found where the experimental conditions are strictly comparable. For example, Vlatkević and Aten⁽⁷⁾ find 36 ± 4 and $49 \pm 1\%$ retention for (presumably) room-temperature thermal neutron irradiations of bromacetic acid, for the isotopes ⁸⁰Br and ⁸²Br. We obtain 53.1 and 47.5%. They have slightly lower results than ours for room-temperature sodium bromacetate. Our figures for yield of methylene dibromide agree well with theirs in the case of the sodium salt, but not in the acid.

In the bromates, chromates and permanganates generally good agreement is obtained^(3,4,5c,8,11a). In lithium nitrate Smith and Aten obtained $51 \pm 4\%$ retention⁽⁹⁾; we have 53.1%. In chromium trioxide Harbottle and Haddock⁽¹⁰⁾ found 79.1% retention against 73.0 here, but the bombardment was much longer in the former case.

Effect of temperature and annealing

If we examine Tables 1 and 2 it may be noted that all compounds studied, except CrO₃, showed the same trend to lower retentions as temperatures were

held to lower values during irradiation, storage and dissolution. This trend has been noted previously⁽¹¹⁾ and appears to be very general. As we mentioned in our preliminary announcements,^(1,2) it clearly implies that until much more work is done on bombardments and analyses at very low temperatures, one will not have trustworthy data which can be used to develop or to test theories (like the "billiard-ball",⁽¹²⁾ "brush-heap"⁽¹³⁾ or "hot-zone"⁽¹⁴⁾ models) which are concerned with the interpretation of recoil-atom product yields in crystals. If we adopt a Vand-Primak⁽¹⁵⁾ picture, i.e. that the annealing processes are distributed over a spectrum of activation energies, these data imply that the spectra are in general so broad that not merely processes which go at or above room temperature ($E_{act} \approx 0.7$ or 0.8 to 1.2 electron volts) but also processes which go at considerably lower temperatures (0 to 0.8 electron volts in activation energy) are present. Potassium permanganate and $Na_2CrO_4 \cdot 4H_2O$ furnish striking examples of this. It is interesting that bromine atoms which have recoiled with very high energies show the same trend ($CH_2BrCOONa$, $(n,3n)$ reaction, Table 2).

If in Tables 1 and 2 one compares the results for the completely room-temperature experiments (bombardment temperatures $\geq 25^\circ C$ and storage temperature $25^\circ C$) with the "quenching" experiments (samples quickly transferred to dry ice after bombardment at $T \geq 25^\circ C$) one can obtain a measure of the room-temperature annealing which follows a hot atom process that also took place at or near room temperature. More direct evidence for rapid room-temperature annealing is given in Table 4.

If one now compares, in Table 2, the retentions in the "quenching" experiment on sodium bromacetate ($R = 26.6$ and 18.3 for ^{80m}Br and ^{82}Br)

with those for the dry ice bombardment ($R = 25.5$ and 18.1) it is noted that there is little effect of the ambient temperature during bombardment upon the yield. The same is true in the fast neutron bombardment of this salt (Table 2).

Annealing effects similar to those presented in Tables 1 and 2 for the parent species ("retention" measurement) are presented in Table 3 for a radiosynthetic product, CH_2Br_2 . Here again yields are found to decrease sharply with decreasing temperature.

The effect of increasing the bombardment time can be seen in the bromacetate yields from the sodium salt, if one compares the samples bombarded for 3 min at -78° , and annealed at room temperature, $+25$ for 2 hours (retentions 32.3 and 24.0%, Table 4 line 3) with those bombarded for 10 sec at room temperature, and annealed the same period (retentions 30.5 and 25.4%, Table 2 line 13). Presumably the crystal bombarded at dry ice temperature "stores up" radiation damage, for example trapped electrons, which then increase the annealing in the ^{80}mBr isotope on warming to room temperature. A similar phenomenon has been observed in the hot-atom chemistry of bromine atoms in C_2Br_6 ⁽¹⁶⁾ and $\text{Ca}(\text{BrO}_3)_2$ ⁽¹⁷⁾ and in K_2CrO_4 ⁽¹⁸⁾.

Although mechanisms for annealing reactions of hot atoms must necessarily be speculative, one can imagine that the increases in $\text{BrCH}_2\text{COO}^-$ and CH_2Br_2 yields in the various samples are the result of recombinations of bromine atoms with radicals such as $\cdot\text{CH}_2\text{COO}^-$ and $\text{CH}_2\text{Br}\cdot$. Spin resonance techniques have demonstrated the presence of $\cdot\text{CH}_2\text{COOH}$ in γ -irradiated crystals of malonic acid.⁽¹⁹⁾ One would expect trapped atoms to become mobile in solids at temperatures $T(^{\circ}\text{K})$ such that the reduced temperature T/T (melting point, $^{\circ}\text{K}$) ≈ 0.4 to 0.6 .⁽²⁰⁾ For bromacetic acid this would be 130 to 194°K ,

both below dry-ice temperature, and for sodium bromacetate around 160 to 250°K, a range which is certainly in the range of our experiments. By analogy one might envision recombination processes involving oxygen atoms in the organon series.

Isotope effects

The experiments presented in Tables 2 and 4 show clearly that the two isotopes of bromine, ^{80}Br and ^{82}Br do not behave identically. Jach and Harbottle have shown^(5a) that in the annealing reactions of bromine atoms in crystalline alkali bromates, ^{82}Br annealed more rapidly than ^{80}Br , coming to a higher plateau. Since the isotopic atoms differ so little in mass, the large differences observed in experiments of the kind reported here must come about as a result of the nuclear process being different, i.e., in differing internal conversion of capture gamma-rays⁽²¹⁾ or different recoil energy. Let us, in the sodium bromacetate system, taking the results for the two isotopes in the liquid-nitrogen bombardment (-195°C, Table 1) as a base line, determine the changes in retention as percentage decreases in the uncombined bromine fraction. Then the ratio of these changes gives a measure of the isotopic effect on annealing. If this ratio be plotted vs the retention of ^{80}Br itself, as a measure of the extent of annealing, the curve presented in Fig. 1 is obtained. This curve shows that in well-annealed samples (larger values of the abscissa) isotopic differences in retention changes have evened out and suggests (although the errors are large) that the largest differences occur in the least-annealed samples. These larger differences would then be related to annealing events having the lowest activation energies, in the Vand-Primak distribution. We are thus led to believe that here the true initial differences in recoil behavior, i.e., in the environments of the hot-atoms

immediately following recoil, with a minimum distortion due to subsequent annealing, are reflected. Clearly more work, involving experiments in which annealing is followed with great precision at low temperature, is needed. If the curve shown in Fig. 1 can be substantiated, it might provide a possible line of explanation for discrepancies in the literature, where different workers have reported isotopic effects of differing degrees. However, even after the overall ratio of changes in retention $\Delta R(80m)/\Delta R(82)$ has approached unity, there still remains a net difference in the retention itself, in sodium bromacetate (35.8% vs 30%).

V. CONCLUSIONS

It would appear from these results, and from others in which low-temperature annealing has been noted⁽¹¹⁾ that, for the time being, we must be prepared to get along without any reliable information on the "primitive", or "intrinsic" yields of hot-atom reactions in crystals except, of course, where those yields are essentially zero. This will continue to be the case until new techniques, perhaps utilizing spin-resonance measurements at low temperature, can be brought to bear on the question "What radioactive species are present after recoil, but before annealing, in a solid?" An extension of existing chemical analytical techniques to lower temperatures is also desirable, but it will probably prove difficult to operate at sufficiently low temperatures.

We may, however, continue to study the course of annealing reactions in solids, and hope that these studies can be correlated with experiments and theory from the field of Solid State Physics, to yield information on diffusion, interstitial-vacancy recombination, lattice relaxation, electron traps and related topics.

- (1) S. R. Veljkovic and G. Harbottle, *Nature* 191, 1287 (1961).
- (2) S. R. Veljkovic and G. Harbottle, *J. Inorg. Nucl. Chem.*, in press.
- (3) K. J. McCallum and A. G. Maddock, *Trans. Faraday Soc.* 49, 1190 (1953).
- (4) G. Harbottle, *J. Chem. Phys.* 22, 1083 (1954).
- (5) a. J. Jach and G. Harbottle, *Trans. Faraday Soc.* 54, 530 (1958).
b. J. Jach, H. Kawahara and G. Harbottle, *J. Chromatography* 1, 501 (1958).
c. G. Harbottle, *J. Amer. Chem. Soc.* 82, 805 (1960).
- (6) E. Glueckauf and J. W. J. Pay, *J. Chem. Soc.* 390 (1936).
- (7) M. Vlatkovic and A. H. W. Aten Jr., *J. Inorg. Nucl. Chem.* 14, 134 (1960).
- (8) H. Sano, *Bull. Chem. Soc. Japan* 33, 1738 (1960).
- (9) R. D. Smith and A. H. W. Aten Jr., *J. Inorg. Nucl. Chem.* 1, 296 (1955).
- (10) G. Harbottle and A. G. Maddock, *J. Inorg. Nucl. Chem.* 5, 249 (1958).
- (11) a. J. W. Cobble and G. E. Boyd, *J. Amer. Chem. Soc.* 74, 1282 (1952)
b. H. Rauscher and G. Harbottle, *J. Inorg. Nucl. Chem.* 4, 155 (1957)
c. L. Lindner and G. Harbottle, "Chemical Effects of Nuclear Transformations" p. 485, International Atomic Energy Agency, Vienna (1961).
d. G. Harbottle, *ibid.* p. 301.
- (12) W. P. Libby, *J. Amer. Chem. Soc.* 62, 1930 (1940).
- (13) J. H. Willard, *Ann. Rev. Nucl. Sci.* 3, 193 (1953).
- (14) a. P. E. Yankwich, *Canad. J. Chem.* 34, 301 (1956)
b. L. Lindner, Thesis, University of Amsterdam (1958)
c. G. Harbottle and N. Sutin, *J. Amer. Chem. Soc.* 62, 1344 (1958).
- (15) a. V. Vand, *Proc. Phys. Soc. (London)* A55, 222 (1943)
b. W. Primak, *Phys. Rev.* 100, 1677 (1955).

- (16) Progress Report, J. E. Willard, University of Wisconsin, dated March 1, 1961.
- (17) A. G. Maddock and H. Muller, Trans. Faraday Soc. 56, 509 (1960).
- (18) A. G. Maddock and J. I. Vargas, Nature 184, 1931 (1959).
- (19) A. Horsfield, J. R. Morton and D. H. Whiffen, Mol. Phys. 4, 327 (1961).
- (20) G. C. Pimentel, in "Formation and Trapping of Free Radicals", Editors A. M. Bass and B. P. Broida, Academic Press (New York) 1960, pp. 75 et seq.
- (21) S. Wexler and T. H. Davies, J. Chem. Phys. 20, 1688 (1952).

Table 1.—The Influence of the Thermal History of a Sample upon its Measured Retention.

Oxyanion Compounds

Compound	Nuclear Process	Bombardment		Storage		Dissolution		Medium	Retention %
		temp °C	time	temp °C	time	temp °C	time		
LiNO ₃	¹⁴ N(n,2n) ¹³ N	-78	15 m	-78	10 m	-60	5 m	Acet	43.9
		+25	15 m	+25	10 m	-60	5 m		53.1
KMnO ₄	⁵⁵ Mn(n,γ) ⁵⁶ Mn	-195	90 m	-195	1 h	-95	15 m	Acet	5.1
		-78	15 s	-78	2 h	-60	10 m		8.9
		+25	15 s	-78	2 h	-60	10 m		15.6
		-78	15 s	-78	2 h	+21	2 m		18.2
		+25	15 s	+25	2 h	-60	10 m		19.3
		+25	15 s	+25	2 h	+2	5 m	H ₂ O	20.7
KMnO ₄	⁵⁵ Mn(p,p3n) ⁵² Mn	+25	15 m-2 h	+25	5 h	-60	10 m	Acet	ca. 18
K ₂ CrO ₄	⁵⁰ Cr(n,γ) ⁵¹ Cr	-195	4 h	-195	1 d	-55	4 h	LiCl	ca. 40
		-78	3 m	-78	3 d	-55	4 h	LiCl	47.2
		-78	3 m	-78	6 d	+2	5 s	H ₂ O	50.0
		+50	3 m	+25	6 d	+2	5 s	H ₂ O	60.4
		+50	3 m	+25	6 d	-55	4 h	LiCl	58.6

$K_2Cr_2O_7$	$^{50}Cr(n,\gamma)^{51}Cr$	- 78	3 m	- 78	1 d	- 55	6 h	LiCl	65.3
		+ 25	7 d	+ 25	6 d	+ 25	15 s	H ₂ O	89.9*
$(NH_4)_2CrO_4$	$^{50}Cr(n,\gamma)^{51}Cr$	- 78	3 m	- 78	1 d	- 55	4 h	LiCl	10.1
		- 78	3 m	- 78	1 d	+ 2	5 s	H ₂ O	14.5
		+ 50	3 m	+ 25	1 d	+ 25	5 s	H ₂ O	17.3
		+ 50	3 m	+ 25	1 d	- 55	4 h	LiCl	16.7
$Na_2CrO_4 \cdot 4H_2O$	$^{50}Cr(n,\gamma)^{51}Cr$	-195	4 h	-195	1 d	- 92	4 h	Acet	32.1
		-195	4 h	-195	1 d	- 55	4 h	LiCl	35.3
		- 78	3 m	- 78	6 d	- 55	4 h	LiCl	39.8
		+ 50	3 m	- 78	1 d	- 55	4 h	LiCl	54.8
		+ 50	3 m	+ 25	6 d	- 55	4 h	LiCl	88.6
		+ 50	3 m	+ 25	6 d	+ 2	30 s	H ₂ O	89.3*
CrO_3	$^{50}Cr(n,\gamma)^{51}Cr$	- 78	3 m	- 78	2 h	- 80	1 h	Acet	69.1
		+ 50	3 m	+ 25	7 d	- 60	30 m	Acet	68.8
		+ 50	3 m	+ 25	7 d	+ 25	5 s	H ₂ O	73.0

* Thermal-column bombardment, flux 6×10^8 n/cm² sec, Ref. 4.

* Single determination, in good agreement with previous results, Ref. 4.

Table 2.—The Influence of the Thermal History of a Sample Upon its Measured Retention.

Compounds Containing Bromine

Compound	Nuclear Process	Bombardment		Storage		Dissolution		Medium	Retention %	
		temp °C	time	temp °C	time	temp °C	time		^{80m} Br	⁸² Br
KBrO ₃	⁷⁹ Br(n,γ) ^{80m} Br	-78	3 m	-78	2 h	+2	1 m	H ₂ O	10.9	12.3
	and	+25	10 s	+25	2 h	+2	1 m	H ₂ O	12.1	13.2
	⁸¹ Br(n,γ) ⁸² Br	+50	10 s	-78	2 h	+2	1 m	H ₂ O	13.3	13.5
		+50	3 m	+25	2 h	+2	1 m	H ₂ O	15.6	16.5
CH ₂ BrCOOH	⁷⁹ Br(n,γ) ^{80m} Br	-195	5 h	-195	2 h	-95	45 m	MeOH-CH ⁻	39.5	34.0
	and	-78	10 s	-78	2 h	-60	15 m	"	42.5	37.4
	⁸¹ Br(n,γ) ⁸² Br	+25	10 s	+25	2 h	-60	15 m	"	53.1	47.5
		-78	10 s	-78	2 h	+2	1 m	H ₂ O-CH ⁻	42.5	37.4
CH ₂ BrCOONa	⁷⁹ Br(n,γ) ^{80m} Br	-195	4 h	-195	2 h	-60	15 m	MeOH	25.0	18.0
	and	-78	3 m	-78	2 h	-60	15 m		25.5	18.1
	⁸¹ Br(n,γ) ⁸² Br	+25	10 s	-78	2 h	-60	15 m		26.6	18.3
		+25	10 s	+25	2 h	-60	15 m		30.5	25.4

(Table 2 continued on next page)

CH ₂ BrCOONa	⁸¹ Br(n,2n) ^{80m} Br	- 78	1.5 h	- 78	1 h	- 60	15 m	MeOH	19.4
		+ 25	10 m	- 78	1 h	- 60	15 m		19.6 /
		+ 25	1 h	+ 25	1 h	- 60	15 m		26.4

Table 3.—The Yield of Organic Bromides in Neutron-Irradiated Bromacetates

Compound	Nuclear Process	Irradiation		Storage		Dissolution		Medium	Organic Yield [‡]	
		temp °C	time	temp °C	time	temp °C	time		⁸⁰ Br	⁸² Br
CH ₂ BrCOOH	(n,γ)	-195	5 h	-195	2 h	-95	30 m	Ether	16.2	16.3
		-78	10 m	-78	2 h	-60	15 m	"	18.5	21.3
		+25	10 m	+25	2 h	-60	15 m	"	31.1	31.2
CH ₂ BrCOONa	(n,γ)	-195	5 h	-195	2 h	-60	15 m	MeOH	2.9	3.2
		-78	3 m	-78	2 h	-60	15 m	"	2.9	3.1
		+25	3 m	+25	2 h	-60	15 m	"	3.3	3.9
CH ₂ BrCOONa	(n,2n)	-78	1.5 h	-78	1 h	-60	15 m	MeOH	3.1	
		+25	1 h	+25	1 h	-60	15 m		3.9	

[‡] The organic bromides are mainly CH₂Br₂. The yield of labeled BrCH₂COO⁻ ion is reported as the "Retention" in Table 2, and is not included in this table.

Table 4.—Effect of Post-Irradiation Annealing upon the Retention

Compound	Nuclear Process	Bombardment		Annealing or Storage		Dissolution		Medium	Retentions %	
		temp °C	time	temp °C	time	temp °C	time		^{80m} Br	⁸² Br
CH ₂ BrCOONa	(n,γ)	-195	4 h	-195	2 h	-60	15 m	MeOH	25.0	18.0
		-78	3 m	-78	2 h	-60	15 m		25.5	18.1
		-78	3 m	+25	2 h	-60	15 m		32.3	24.0
				+45	1 m				31.8	26.8
				+45	3 m				33.1	27.6
				+45	11 m				35.8	30.0
		+50	3 m	-78	2 h	-60	15 m		30.0	19.5
		+50	3 m	+25	2 h	-60	15 m		33.5	26.2
		+25	10 s	+25	2 h	-60	15 m		30.5	25.4
CH ₂ BrCOONa	(n,2n)	-78	1.5 h	-78	1 h	-60	15 m	MeOH	19.4	
		-78	1.5 h	+25	2 h	-60	15 m		24.0	
				+54	3 m				24.0	
				+54	11 m				39.3	
		+25	10 m	-78	2 h	-60	15 m		19.6	
		+25	1 h	+25	2 h	-60	15 m		26.4	

$(\text{NH}_4)_2\text{CrO}_4$	(n, γ)	- 78	3 m	- 78	1 d	- 55	4 h	LiCl	10.1
		- 78	3 m	*		+ 2	5 s	H ₂ O	14.5
$\text{K}_2\text{Cr}_2\text{O}_7$	(n, γ)	- 78	3 m	- 78	1 d	- 55	6 h	LiCl	65.3
		- 78	3 m	- 78	1 d	- 20	2 h	LiCl	67.5
		- 78	3 m	*		+ 2	30 s	H ₂ O	71.9
$\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$	(n, γ)	- 78	3 m	- 78	6 d	- 55	4 h	LiCl	39.8
		- 78	3 m	*,**		+ 2	30 s	H ₂ O	47.3
				+ 20	1 m	+ 2	30 s	H ₂ O	54.1
				+ 20	3 m				58.9
				+ 20	10 1/2 m				58.1
				+ 20	35 m				64.2
				+ 20	27 h				79.0

* In this experiment, annealing only occurred during the period of warmup and dissolution: i.e., the sample was transferred from its container at -78°C into water at +2 and dissolved as quickly as possible.

** This, and the following experiments are single determinations, to which an error of about ±2% should be attached.

Fig. 1. Ratio of retention changes for the two isotopes ^{80m}Br and ^{82}Br in the annealing of bromine species in sodium bromacetate versus degree of annealing as measured by ^{80m}Br retention.

END