may become important at the very high temperatures. Although the general chain photodecomposition scheme suggested by Sieger and Calvert[3] is in accord with this work, the specific reactions 1 and 2 appear unlikely; a careful analysis of the products of run 46 and 54 failed to reveal detectable quantities of CF_3COCF_3, although the method of analysis was sufficiently sensitive to find even 5% of the total quantity expected from the reaction scheme. There is no obvious alternative mechanism to replace 1 and 2. The undefined reaction sequence

$$CF_3 + CH_3COCF_3 \longrightarrow X \longrightarrow CH_3 + \text{non-volatile products} \quad (24)$$

must be subjected to further experimentation. The absolute magnitude of the quantum yields of products of run 54 differ from those found by Sieger and Calvert[3] using a different photolysis system but under similar conditions of temperature, pressure, wave length and at a slightly higher light intensity; for example, Φ_{CO} was 1.95 compared to 7.42 found in this work. The variability of the length of the chain process with change in reaction system coupled with the fact that homogeneous reactions similar to 1, 2, 3, 23 and 24 have not been observed in analogous systems, suggest strongly that these chain steps are at least in part heterogeneous reactions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Comparison of the Organic Products from the Br^{80m} (4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80} (18 min.) Process in the Propyl Bromides with Those from the $Br^{79}(n,\gamma)Br^{80}$ Process

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It has been shown previously that activation of Br_2 by the (n,γ) and by the isomeric transition processes in solutions of Br_2 in CCl_4 yields the same distribution of organic products. The present paper shows a similar result for five products (CH_2Br_2, C_2H_5Br, n-C_3H_7Br, i-C_3H_7Br and 1,2-$C_3H_6Br_2$) from the (n,γ) and I. T. activation of bromine in n-C_3H_7Br and i-C_3H_7Br, thus lending support to the conclusion that the product determining steps are the same for the two methods of activation.

Introduction

The $Br^{79}(n,\gamma)Br^{80}$(4.4 hr. and 18 min.) and $Br^{81}(n,\gamma)Br^{82}$(36 hr.) processes yield product atoms with a recoil energy sufficient to break chemical bonds[2] (some 4000 kcal. per mole if all of the nuclear energy is lost as one photon) and, in at least an appreciable fraction of the events, a positive charge.[3] The isomeric transition of $Br^{80m}(Br)^{80m}$(4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80}(18 min.)) gives daughter atoms with an average charge[4] of +10. This charge may spread over the parent molecule and as a result of coulombic repulsion cause the bromine atom to split out with considerable kinetic energy (about 80 e.v. in the case of Br_2 with +10 charge). In liquid or solid organic media bromine atoms which have ruptured their parent bonds as a result of either the (n,γ) process or the isomeric transition process are able to enter organic combination, apparently by producing a random fragmentation[2] of bonds in the surrounding molecules and combining with radicals so formed. From the available facts about such processes it is impossible to say whether the kinetic energy or the energy from charge neutralization, or both, are primarily responsible for the chemical fate of the tagged atom, although it has been customary to assume that recoil energy is the important factor in (n,γ) activation and charge in activation by isomeric transition.

If the determining factor in chemical activation by the two processes is the same, the distribution of chemical products would be expected to be the same in the same chemical system; if the activating step is different, the product distribution might be different. It has been shown[5] that the ratios of CCl_3Br to CCl_2Br_2 and to higher boiling components in the organic products from the (n,γ) and isomeric transition processes of Br_2 in CCl_4 are identical within the accuracy of the determinations. This is not, however, conclusive evidence that the mechanism of chemical activation is the same for the two processes. It may be that the possible types of bond rupture in a simple molecule like CCl_4 are so few that fragmentation occurs in an identical fashion whether it results from charge neutralization processes or from the dissipation of recoil energy. It was therefore important to test more complex molecules than the Br_2–CCl_4 system. In the work reported below normal and isopropyl bromide have been chosen for this purpose because the yields of a variety of products from the (n,γ) process on these compounds have been studied carefully.[6,7]

Experimental

Liquid Br_2 irradiated in the CP5 pile of the Argonne National Laboratory at a flux of 2×10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$

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(2) For reviews of the literature on chemical effects of nuclear transformations see: J. E. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953); J. E. Willard, *Ann. Rev. Phys. Chem.*, **6**, 141 (1955).

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TABLE I

COMPARISON OF YIELDS OF INDIVIDUAL PRODUCTS FROM THE REACTIONS ACTIVATED BY THE (n,γ) AND ISOMERIC TRANSITION PROCESSES OF BROMINE IN PROPYL BROMIDES

	Organic yields from i-C_3H_7Br, %^{a}				Organic yields from n-C_3H_7Br, %^{a}	
	Unscavenged^b		Scavenged^b		Scavenged^b	
	$(n,\gamma)^7$	I. T.	$(n,\gamma)^7$	I. T.	$(n,\gamma)^7$	I. T.
C_2H_5Br	0.14		0.10	0.69	0.30	0.53
i-C_3H_7Br	10.1	11.9, 8.2, 9.6	5.6	4.9, 4.5 5.0, 4.8	0.73	0.78
n-C_3H_7Br	1.0	3.8, 2.7 2.1	0.66	0.79	7.7	7.9, 8.1 7.8, 7.1
CH_2Br_2			0.55	1.08	0.95	1.9
1,2-$C_3H_6Br_2$			3.8	3.9	2.29	4.7
Total organic	23.6	22.0, 22.8 19.5	16.9	16.8, 16.1, 17.8 16.4, 15.0	21.0	22.4, 21.2 22.0, 17.4

^{a} % of total $Br^{79}\,(n,\gamma)Br^{80m}$ or $Br^{80m} \xrightarrow{\text{I. T.}} Br^{80}$ events. ^{b} The "scavenged" samples contained 5×10^{-2} mole fraction of Br_2 during the reaction period. The unscavenged I. T. samples contained 5×10^{-5} or 5×10^{-4} mole fraction of Br_2. The latter concentration had been shown[7] to lower the organic yield by only 10–15% of its unscavenged value in n-C_3H_7Br and by less in i-C_3H_7Br.

for a few hours was added in known concentration to purified normal or isopropyl bromide and the mixture was allowed to stand in the dark for about three hours to allow the reactions activated by the isomeric transition to take place. The Br_2 was then extracted with aqueous sulfite, following which the organic liquid was washed with water, dried by passing through anhydrous $MgSO_4$ on filter paper, mixed with one or more carrier liquids (inactive portions of compounds suspected of being formed in tracer concentrations by the isomeric transition process), and distilled through a 1″ i.d., 1′ long column packed with glass helices. From the counting rates of the aqueous extract, of the organic liquid prior to distillation, and of the various cuts from the distillation, the yield of each species for which carrier was added was computed after appropriate corrections for decay, and differences in density of the counting media.

Because of the short (18 min.) half-life of the products, distillations were done rapidly (40 ml. in about 30 min.), and consequently the separations were imperfect. By use of only two carriers at a time it was possible to determine the composition of each cut from its refractive index and an experimentally determined plot of refractive index *vs.* composition. A plot of the compositions of the several cuts *vs.* specific activity then gave a straight line (if there were no organic products which boiled between the two carriers) which could be extrapolated to 100 mole % for each component, thus giving the specific activity of each component. On such a plot most of the points fell on a straight line, except for those representing the first two or three cuts which sometimes showed a high activity due to a lower boiling species being removed. When the refractive index method was not applicable an attempt was made to obtain a sufficiently good separation to give cuts of constant specific activity—in some such cases where the component was much lower in specific activity than that which preceded it, it was only possible to set a maximum value.

It was essential that the propyl bromides used be sufficiently free from olefin type impurities so that very little of the Br^{80m} (4.4 hr.) would become organically bound. The amount so bound was usually less than 0.2%. Such organically bound 4.4 hr. bromine would produce (18 min.) activity in the still during the distillation and so distort the product spectrum. Adequate purity was obtained by a combination of prolonged mechanical stirring with concd. H_2SO_4, distillation, and pretreatment with Br_2.

The solutions were counted in thin-walled glass annular jackets placed around an Amperex 90 NB metal wall Geiger tube. Use of the equipment and procedures described above to determine the yields of selected products resulting from (n,γ) activation of propyl bromides gave excellent agreement with values obtained in previous work[6,7] where better separations were possible because speed was not required.

Results and Discussion

In all cases the absolute values of the yields obtained from the isomeric transition in this work (Table I) are within a per cent. or so of those from the (n,γ) process obtained in previous work. This applies to product molecules identical with the solvent and to their isomers; to C_2H_5Br, which requires the rupture of a carbon–carbon bond and replacement of a bromine atom; to CH_2Br_2, which requires the rupture of a carbon–carbon bond and replacement of a hydrogen atom; and to 1,2-dibromopropane, which requires H atom replacement on the solvent molecules; it applies both to the unscavenged reaction ("hot" plus "thermal" processes[2]) and to the scavenged reaction (hot process only). Although there are no large differences in the absolute values of the yields of the products of the isomeric transition as compared to the (n,γ) process, the ratio of the former to the latter for certain products with low yields is considerably greater than unity (*i.e.*, for n-C_3H_7Br from i-C_3H_7Br without scavenger; for CH_2Br_2 from both i-C_3H_7Br and n-C_3H_7Br with scavenger; and for $C_3H_6Br_2$ from n-C_3H_7Br with scavenger). There is a possibility that these variations are due to experimental error of the determinations. If they are not, they may result from the fact that the Br^{80} (18 min.) atoms from the isomeric transition were born with Br_2 as the mother molecule whereas C_3H_7Br was the parent species for the activated atoms from the (n,γ) process. In the former case a second Br atom is always close to the activated atom at the time of reaction and may cause a somewhat different product distribution than if the parent were C_3H_7Br. It seems rather improbable that a difference in the mode of activation ((n,γ) as compared to I. T.) would cause these observed differences in yield when it does not cause a difference in the total organic yields or in the major features of product distribution.

Br_2 rather than C_3H_7Br was employed as the source of the Br^{80m}(4.4 hr.) in order to make it possible to separate the latter from the organic mixture completely before distillation, and to observe only Br^{80m}(18 min.) counts in the distillate.

It has been demonstrated[8] that when bromine atoms undergo isomeric transition they may sometimes fail to rupture the parent bond and that the extent of this failure varies with the nature of the

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[8] R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **74**, 6213 (1952).

parent molecule. This is a small effect and would not be expected to appreciably influence organic yield results of the type reported here.

On the basis of the data of Table I it may be concluded that activation of bromine by isomeric transition in the propyl bromides results in the same products and with much the same yields as the (n,γ) process. The conclusion is the same as that for the Br_2–CCl_4[5] system, but unlike the latter cannot be explained away by the hypothesis that the molecules are so simple that no alternatives to the same product yields are possible. It strongly suggests that in the liquid propyl bromides the chemical reactions following the (n,γ) and the isomeric transition processes are due to the same cause, *i.e.*, either kinetic energy, or charge neutralization, or a combination of the two.

Recent work has demonstrated that the organic yields from the (d,p), (n,2n) and (γ,n) reactions on iodine in the alkyl iodides[9] are the same as those from the (n,γ) reaction,[10] thus establishing the fact that the magnitude of the initial recoil energy of the atoms (above some minimum) does not affect their chemical fate. The simplest hypothesis to explain the identity of yields obtained from the (n,γ) and I. T. processes on bromine and from the (n,γ), (γ,n), (d,p) and (n,2n) processes on iodine is that kinetic energy is responsible for the reaction in all cases. The tagged atom may enter stable combination either by reaction with one of the radicals it has formed in losing its energy or by a "hot" bimolecular step.[11] Kinetic energy in excess of that required for the "hot" reaction or for forming the last few radicals in the path is either dissipated too far away from the site of thermalization of the tagged atom to affect the yield, or forms radicals with the same spectrum of types as those formed by the last of the energy dissipated.

The distribution of charge among atoms formed as a result of internal conversion in the I. T., (n,γ), (d,p) and (n,2n) processes is presumably different for the different nuclear processes. Since in the systems cited above the organic yields from these processes are the same, it appears that the initial charge does not make a difference in the yield. Further support is given to this conclusion by coupling the evidence that the $Br^{79}(n,\gamma)Br^{80m}$ (4.4 hr.), $Br^{79}(n,\gamma)Br^{80}$ (18 min.) and $Br^{81}(n,\gamma)Br^{82}$ processes give different yields of charged atoms,[3] with evidence that the organic yields from these processes are the same.[12] Possibly complete charge neutralization occurs in all cases before the kinetic energy is lost.

Early exploratory work[13] on mixtures of Br_2 and C_2Cl_4 gave organic yields of 37% in solution and 0% in the gas phase when the bromine was activated by the (n,γ) process, in contrast to 85% in the solution and 19% in the gas phase when activation was due to isomeric transition. Prompted by the results of the present paper, we have repeated these earlier tests, using the better techniques and higher counting rates now available. We obtain organic yields of 50 ± 2% for both $Br^{79}(n,\gamma)Br^{80m}$(4.4 hr.) and I. T. activation in 0.7 mole % solutions of Br_2 in liquid C_2Cl_4. Four experiments on gaseous mixtures of 15 mm. of C_2Cl_4 and 15 mm. of Br_2 have all given organic yields of less than 2.5% by I. T. activation. This value is in agreement with the low yields usually[2] (though not always[11]) observed for (n,γ) activation in gaseous systems and with that observed for (n,γ) activation on the Br_2–CCl_4 system in the previous tests.

In contrast to the above results there are at least two reports in the literature of different organic yields from the I. T. and (n,γ) activations of bromine. The most striking is that of bromine reacting with toluene for which it has been reported[14] that the toluene bromide/benzyl bromide product ratio is 0.12 when activation is by isomeric transition and 0.8 when it is by neutron capture. The other is the observation[15] that the organic yield of Br^{80}(18 min.) from the isomeric transition of CCl_3Br^{80m} in CCl_3Br is about 15 absolute % higher both in the liquid and solid states than the corresponding (n,γ) yield.

In summary it may be said that analyses of the products of the reactions of bromine activated by both the I. T. and (n,γ) processes in the propyl bromides show remarkable similarity for the two methods of activation. No explanation is available for the contrast between these results and those cited in the last paragraph above.

In seeking to interpret these phenomena it would be helpful to have more information than is now available on the physical processes involved, including data on the complete γ-ray spectra from the (n,γ) process, the timing of γ emissions relative to internal conversion in the (n,γ) process, the fraction of the atoms which undergo internal conversion in the (n,γ) process and their charge distribution, the charge distribution of the atoms from the I. T. process, and more information on energy transfer and charge transfer processes in solution.

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