JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 84 JULY 17, 1962 NUMBER 13

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Competitive Reactions of Recoil Tritium Atoms in Liquid Mixtures[1]

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RECEIVED OCTOBOR 2, 1961

The chemical reactions of recoil tritium atoms from $Li^6(n,\alpha)H^3$ have been studied in mixtures of solvents containing low concentrations of LiBr. The ratio of the specific radioactivities of aromatic and aliphatic components varies as much as a factor of 4 as the volume fractions of each are varied from 0.025 to 0.0975. This variation is caused almost entirely by an increase in the specific tritium radioactivity of the aromatic ring at low mole fractions of the aromatic component and has been observed both for aniline and benzoic acid in mixtures with ethanol and acetone. The experimental observations are consistent with a model for competitive recoil tritium reactions that assumes the energetic reactions occur with single molecules, independent of neighbors, and in proportion to the concentration of each molecular species. The relative probabilities of T for H substitution vary with the energy of the tritium, but the fraction of bond-forming interactions and the energy degradation spectrum in non-bonding interactions are generally similar for all molecules in the higher kinetic energies.

Recoil tritium atoms are able to replace hydrogen atoms bonded to essentially all carbon-atom types with roughly comparable ease, as shown by both intramolecular and intermolecular determinations of tritium distribution.[4] These hydrogen replacements have been shown in numerous experiments to take place primarily at energies above thermal energies in direct substitution processes. Inequalities in the specific radioactivity of different non-labile hydrogen positions in the same system have demonstrated that preferences do exist for the occurrence of these substitution processes, despite the large energies available at the time of chemical bond formation for the tritium atom. The experiments reported here have been performed to investigate more carefully the competition of different bond-types in recoil tritium reactions.

The competitive reactions involved here have all been of the nature

$$\mathrm{T} + {\equiv}\mathrm{C{-}H} \longrightarrow {\equiv}\mathrm{C{-}T} + \mathrm{H} \qquad (1)$$

with no other change in the chemical identity of the parent molecule. They have been intermolecular in nature, carried out in liquid solutions of soluble lithium salts, and have been extended over the full range of mole fractions of the two competing reactants. Aliphatic–aromatic competitions have been carried out with several pairs of solvents, and the aliphatic competition with H_2O has also been studied. In the latter case, the reaction directly competing with (1) is the energetic substitution for H bonded to oxygen and cannot readily be measured because of the lability of the hydrogen–oxygen bond and because HTO can also be formed by thermal reactions.

Experimental

Tritium Production.—The recoil tritium atoms were formed in each solution by thermal neutron irradiation of Li^6 present as soluble lithium bromide. (Tritium production rate = 1.9×10^5 d.p.m., tritium/mg. LiBr/hr./10^{12} flux.) The mixtures were chosen to provide a variety of C–H bond types while still maintaining sufficient solubility for the lithium salt. The acetone–ethanol series was irradiated for 1 hr. at a flux of 1.8×10^{12} neutrons/cm.^{2}/sec. at the Brookhaven reactor. The other samples were nominally irradiated at Argonne CP-5 for approximately 12 hr. in a flux of 1×10^{12} n./cm.^{2}/sec. The actual neutron exposures varied from this by as much as a factor of two as pile operations and concurrently irradiated samples required. All of the samples for a given series received a common irradiation exposure except for the flux variations over centimeter distances in the reactor.

Preparation of Solutions.—Solutions were prepared by mixing the appropriate volumes of dilute LiBr solutions in the respective pure liquids. For each series, the LiBr concentration in each component was equal when measured in grams per ml. Solutions were prepared over the entire range of mole fractions with special emphasis in the later

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(1) Research supported by A.E.C. Contract No. AT-(11-1)-407.

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(4) See, for example, J. K. Lee, B. Musgrave and F. S. Rowland, *J. Am. Chem. Soc.*, **82**, 3545 (1960), or the recent papers by the same authors and by R. Wolfgang, *et al.*, in the Proceedings of the I.A.E.A. Symposium on the Chemical Effects of Nuclear Transformations, Prague, 1960.

series on the two mole fraction extremes. The series included:

Aniline–acetone

Series I	0.382 g. LiBr/100 ml.
Series II	0.359 g. LiBr/100 ml.
Series III	0.330 g. LiBr/100 ml.

Acetone–ethanol

5.14 g. LiBr/100 ml.

Acetone–water

0.359 g. LiBr/100 ml.

Aniline–ethanol

0.286 g. LiBr/100 ml.

The acetone was spectroquality reagent, used without further purification. Aniline was distilled twice under diminished pressure and the fraction boiling between 53.0–53.5° at 3 mm. was used. Absolute ethanol and reagent-grade lithium bromide were used.

Several benzoic acid–acetone samples were prepared by direct mixing of a measured volume of acetone with weighed quantities of LiBr and benzoic acid. The solubility of benzoic acid limited this series to low mole fractions of benzoic acid. The composition was always 0.50 of g. LiBr per mole of total organic compound.

The solutions were sealed in quartz ampules approximately 20 cm. long, 10 mm. i.d. Most samples were evacuated with the contents frozen prior to sealing, but some tubes from most series were sealed while air-saturated. All solutions containing aniline darkened somewhat during irradiation.

Isolation of Pure Components as Solid Derivatives.—Each irradiated liquid sample was cooled with liquid nitrogen prior to opening to facilitate release of excess gas. A preliminary separation of aniline and ethanol was made by 0° distillation of the ethanol from the acidified contents of the irradiated ampule. The irradiated acetone–aniline solutions were stored over charcoal for 30 minutes and then filtered before aliquots were taken. Acetone was first separated from benzoic acid by distillation. Aliquots of each solution were then transferred for preparation of a suitable solid derivative. These derivatives were chosen for convenience in preparation and freedom from exchange of carbon-bonded tritium with solvent.

The initial assay of radioactivity was routinely performed on the product from the third successive recrystallization of the derivative. Additional recrystallizations were then carried out until the tritium measurements showed that no further activity was being removed by the processing. Most of the precipitates proved to be radiochemically pure in the first crystallization assayed. The melting point was within 0.5° of that for the authentic compounds for all samples by the end of the third recrystallization.

The 3,5-dinitrobenzoate and 2,4-dinitrophenylhydrazone have previously been demonstrated to undergo negligible tritium exchange with the solvent during derivative formation.[5] Acetanilide was prepared from an artificial mixture made by adding 10 volume % aniline to an irradiated acetone–LiBr solution. The specific radioactivity of this aniline was approximately 0.3% that of the acetone from the same solution, or 10^{-3} times the specific activity that was observed when aniline was present in the same concentration during the irradiation.

Acetone as the 2,4-Dinitrophenylhydrazone.—Acetone-2,4-dinitrophenylhydrazone was precipitated from an acidified aqueous solution by the addition of a hot, acid, methanolic solution of 2,4-dinitrophenylhydrazine. Recrystallization was carried out from aqueous methanol or ethanol.

Aniline as Acetanilide.—Irradiated solutions containing aniline were added to aqueous HCl and decolorized with charcoal. Acetone was partially removed by distillation from solutions in which its concentration greatly exceeded that of the aniline. Acetic anhydride was then dissolved, and acetanilide precipitated by addition to sodium acetate solution. The acetanilide was recrystallized from 10% dioxane–water solution.

Ethanol as the 3,5-Dinitrobenzoate.—The ethanol-3,5-dinitrobenzoate was prepared by heating the chloride and the irradiated solution on the steam bath for five minutes. After cooling and solidification, 3% $NaHCO_3$ solution was added, heated and filtered off. The derivative was extracted with hot ethyl ether and evaporated to dryness. The precipitate was then recrystallized from a dilute methanol solution after treatment with Darco charcoal.

Benzoic Acid.—Benzoic acid was purified directly without derivative formation. Three successive recrystallizations from aqueous solutions treated with Darco charcoal sufficed to give crystals with the proper melting point.

Assay of Radioactivity.—Small aliquots of each solid sample were converted to gas by the zinc-fusion combustion technique and counted in a gas phase proportional counter in the presence of 40 cm. of propane.[6]

The earlier measurements of the radioactivity of the acetone-2,4-dinitrophenylhydrazone in aniline solutions showed much higher specific activity at low mole fraction of acetone. This radioactivity was not removed by additional crystallizations but was readily removed upon decomposition and regeneration of the phenylhydrazone. Distillation separation of the acetone before derivative formation also removes this impurity. The contamination presumably came from a radioactive product of tritium reactions with aniline and was not removed by crystallization because of its similarity to the phenylhydrazine reagent. At the lowest mole fractions of acetone in aniline, this impurity activity more than doubled the apparent acetone specific activity.

Results

The recoil tritium activity found in a particular chemical form after irradiation of two molecules in competition with each other can be expressed in terms of the total radioactivity, as shown in Fig. 1 for the mixtures of aniline and ethanol. The total radioactivity bonded into non-labile positions in a particular molecule rises monotonically with its increasing mole fraction in all of the systems investigated here, confirming the rough equality of tritium substitution for hydrogen in several types of carbon–hydrogen bonds.

The same data of Fig. 1 are plotted in Fig. 2 on the basis of the specific radioactivities of each of the two organic components of the solutions. The rising total tritium content of ethanol is approximately proportional to its mole fraction as shown by the constant specific radioactivity. While the total aniline radioactivity is also rising with mole fraction, the specific radioactivity of the aromatic ring is consistently greater as its mole fraction is lowered and varies by as much as a factor of 3 in Fig. 2. The presence of air in one solution has a negligible effect on the results.

Similar results are shown in Fig. 3 for the mixtures of aniline and acetone of series I and II. No acetone results are included for series I, since the impurity difficulties mentioned previously under assay of radioactivity had not yet been removed. Figures 4 and 5 illustrate the results obtained from acetone–water and acetone–ethanol solutions, respectively.

Several series of measurements in the range of low aromatic concentration are compared in Fig. 6. Again, the presence of air during the irradiation has a negligible effect on the observed specific activities of the component molecules. The specific activity of benzoic acid also rises with decreasing mole fraction, although the molar specific activity ratios are lower than those found for aniline at comparable ratios of phenyl groups to acetone molecules.

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(5) W. J. Hoff, Jr., and F. S. Rowland, *J. Am. Chem. Soc.*, **79**, 4867 (1957).

(6) F. S. Rowland, J. K. Lee and R. M. White, "Oklahoma Conference—Radioisotopes in Agriculture," TID-7578, U. S. Government Printing Office, 1960.

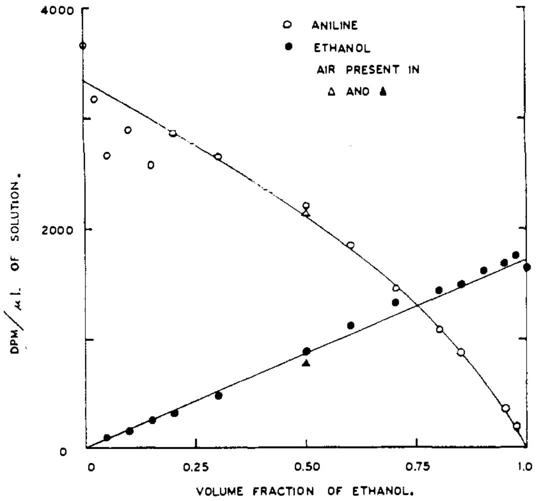

Fig. 1.—Total non-labile radioactivity as acetone and aniline from recoil tritium reactions in LiBr solutions.

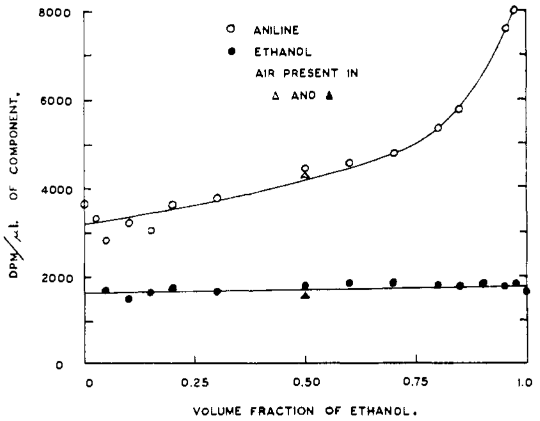

Fig. 2.—Non-labile specific radioactivity of aniline and ethanol from recoil tritium reactions in LiBr solutions.

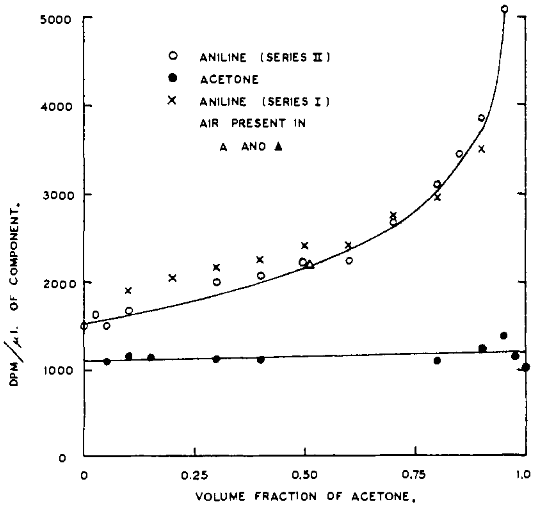

Fig. 3.—Non-labile specific radioactivity of aniline and acetone from recoil tritium reactions in LiBr solutions.

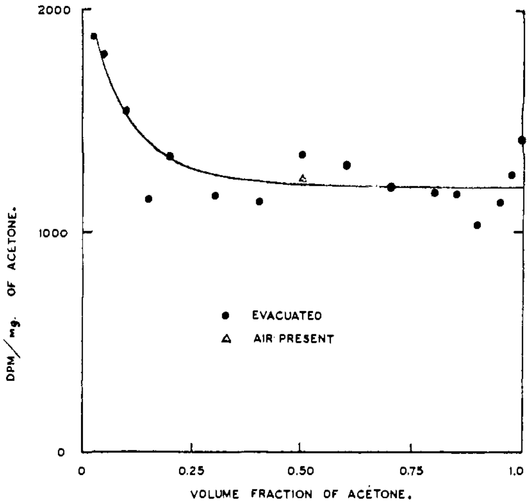

Fig. 4.—Specific radioactivity of acetone from recoil tritium reactions in acetone–water solutions of LiBr.

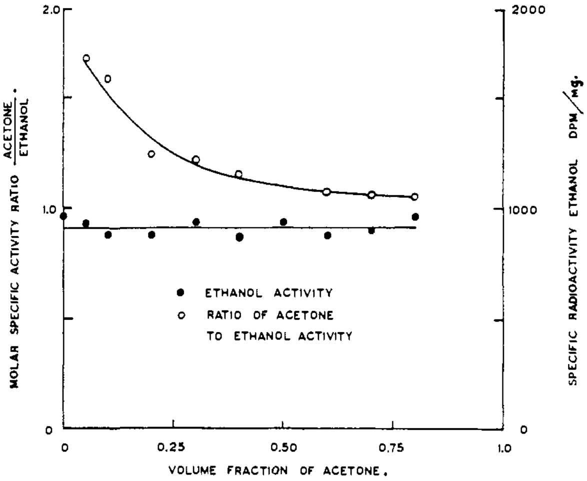

Fig. 5.—Molar specific activity ratios for recoil tritium reactions in acetone–ethanol mixtures.

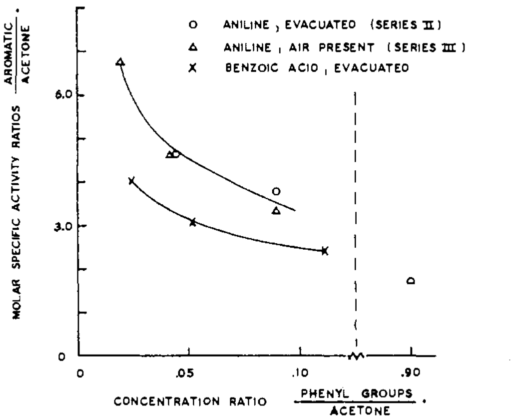

Fig. 6.—Molar specific activity ratios for recoil tritium reactions in acetone–aromatic compound mixtures.

The over-all accuracy of the measurements is adequately illustrated by the scatter of the points. Although uniform neutron fluxes were sought for all samples of a series, the specific radioactivity undoubtedly varies somewhat from ampule to ampule because of inhomogeneity in the neutron intensity. This factor cancels out when ratios of specific activities are compared, as in Figs. 5 and 6.

Discussion

Simple Model for Competitive Tritium Reactions.—The initial energy of the recoil tritium atom far exceeds the energies at which chemical reaction with stable bond formation can take place, and most of this kinetic energy must be lost before such reactions are possible. The actual bond formation for the tritium can take place in one of the encounters occurring as the atom descends down the last stages of the kinetic energy scale. If the remaining extra energy is lost without reaction in the "chemical bond energy range," the tritium may then react as a thermal atom. The mechanisms[7] and energetics[8] dominant in a variety of recoil tritium systems suggest that the tritium atom usually forms a stable bond in interactions above thermal energies, probably in the range of a few electron volts. The substitution of tritium for hydrogen is one of the most important of energetic reactions occurring for recoil tritium and always accounts for an appreciable fraction of the total tritium formed in the system.

A simple model for these competitive high kinetic energy reactions can then be set up on the basis of the assumptions:

(1) The energetic reactions involve interaction with only one molecule at a time, and these reactions are independent of the identity or presence of nearby neighbors.

(2) The total probability of interaction with the various molecules in the system at each energy is proportional to the number of each present, appropriately weighted by some factor such as molecular size.

(3) The total probability of all bond-forming reactions is the same fraction of the total reaction cross-section for all molecules at each energy.

(4) The energy loss spectrum of tritium atoms in non-reacting interactions with all molecules is the same.

(5) The relative probabilities of all high energy bond-forming reactions are constant throughout the high energy range in which the bulk of the substitution processes take place.

The most important predictions from such a model for the experiments described here are then that (a) the fraction of the total tritium activity found in a given radioactive molecule will be linearly proportional to the weighted fraction of the molecule from which it is formed in the irradiated mixture (the weighting factor being that chosen under (2) above); (b) the ratios of specific radioactivity for substitution into two components of the solution will be independent of the composition of the solution; and (c) the specific radioactivities of two molecules furnish a relative measurement of the probabilities of two high energy reactions. If the total tritium activity formed in the system is held constant as concentrations are varied, the absolute specific activities, as well as the ratios of them, will be independent of concentration in the mixture.

The first assumption implies that the closeness of neighbors in the liquid state has no effect on the nature of the energetic substitution of tritium for hydrogen. Examination of the qualitative and quantitative nature of the radioactive products in both gaseous and liquid phases suggest that this assumption is a reasonable approximation for tritium systems.[4,9,10] The presence of LiBr in the solutions is ignored since it is present in low concentrations and the tritium is assumed to undergo energetic reaction with all species in approximate proportion to the amount present.[11] The experimental observations which differ from the predictions of this model will then be discussed in terms of the failure of the oversimplified assumptions (3) to (5).

Dissolved oxygen generally diverts all reactions involving free radicals into more oxygenated species, with a consequent alteration of radioactivity distributions. Such variations have been recorded for some tritiated products in other recoil tritium liquid phase systems, always for molecules logically involving free radical precursors.[10] The lack of effect of dissolved air on the per cent. tritium incorporation in any of the C–H bonds measured here strongly supports the premise that the substitution of T for H occurs almost entirely above thermal energies, *i.e.* involving reactants so fleeting in life time that they do not encounter free radicals even in an unscavenged system.

Although the graphs of Figs. 1–6 show clear evidence of disagreement with the simple model above, some emphasis should be placed first on the fact that there are no disagreements observed as large as a factor of 10 and most are much less than this. The frequent observation in thermal systems of hydrogen atom reaction rates differing by factors of 10^2 to 10^4 or greater have no parallel in the reactions of these energetic tritium atoms. While geometric or steric control of reaction probabilities can discriminate between various types of bonded hydrogen, the probabilities of competing reactions are much less dissimilar than many typical observations in which activation energies are controlling the reaction path.

Specific Radioactivity *vs.* Mole Fraction.—The total tritium activity of ethanol shown in Fig. 1 and the constant specific radioactivity of ethanol shown in Figs. 2 and 5 and of acetone in Fig. 3 are in agreement with the simple competitive predictions. The intercepts for pure acetone and ethanol solutions represent approximately 27 and 23% of the total tritium radioactivity formed in each solution,[12] while the substitution into the aniline

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[7] For example, the retention of configuration in substitution for hydrogen at asymmetric carbon atoms, as reported in M. Henchman and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2991 (1961); J. G. Kay, R. P. Malsan and F. S. Rowland, *ibid.*, **81**, 5050 (1959).

[8] For example, the pressure-dependent gas phase isomerization of labeled cyclopropane to propylene discussed in J. K. Lee, B. Musgrave and F. S. Rowland, *Can. J. Chem.*, **38**, 1756 (1960), and others mentioned in ref. 4.

[9] A. M. Elatrash, R. H. Johnsen and R. Wolfgang, *J. Phys. Chem.*, **64**, 785 (1960).

[10] K. C. Lee, Burdon Musgrave and F. S. Rowland, unpublished work.

[11] T. Kambara, R. M. White and F. S. Rowland, *J. Inorg. Nuclear Chem.* (in press), have demonstrated that various salts in dilute aqueous solution have a negligible effect on the reactions of recoil tritium with water.

[12] The equivalent percentages given in ref. 5 are 25 and 22%. In all cases, the percentages were measured *versus* the expected total

molecule in pure aniline solutions accounts for about 52% of the total tritium. In each case, the replacement of hydrogen by tritium in an energetic substitution accounts for an important fraction of the total amount reacting non-thermally. However, tritium atoms in labile combination in each system make the total fraction reacting while above thermal energy difficult to estimate.

The specific activity of aniline in mixtures with ethanol and acetone is much higher when the aniline is in low concentration and is not in agreement with the predictions of the simple model. Obviously, replacement of the hydrogen bonded to the aromatic ring has become relatively more probable per hydrogen atom when the aromatic rings are in low concentration. Since this increase in probability has not been accompanied by any diminution in the ability of tritium to substitute into the CH_3– or –CH_2– groups of acetone and ethanol, the excess radioactivity of the aniline must have been gained at the expense of some other reactions. This "scavenging" action of the aromatic ring must be non-thermal in nature since it involves the T- for H- substitution, which is not observed thermally at these temperatures.

Variation in Relative Probability of Energetic Reactions *vs.* Kinetic Energy.—The aniline specific radioactivity of Figs. 2 and 3 can be satisfactorily explained if assumption 5 is replaced by a set of relative probabilities, illustrated in Fig. 7, in which the substitution for aniline (11) is favored over acetone (1) at lower kinetic energies. In such a case, the tritium atoms which react at higher energies substitute into both aniline and acetone. A certain fraction, of course, fail to react at high energies and fall to the lower energies for which reaction with aniline is more and more highly favored over acetone. If several encounters or more are required to pass through this lower part of the range without reaction, much of the tritium will become fixed by the aniline, and the specific radioactivity will be highest for the concentrations in which the number of unlabeled aniline molecules is the smallest.

The effect of the aromatic ring in the benzoic acid–acetone mixtures of Fig. 6 is quite similar to the effect in aniline. The lowered efficiency of benzoic acid in gaining *excess* specific activity, per phenyl ring, probably results from greater simultaneous competition with the carbonyl oxygen plus hydroxyl group than with the amino group of aniline. The specific activity of acetone in both ethanolic and aqueous solutions also rises in lower mole fractions, to a lesser extent than with aniline, and can result from a similar favored competition for the lower energy reactions.

Energy Loss Spectrum; Fractional Probability of Bond Formation.—The experimental consequences of failure of either assumption 3 or 4 of this model are quite similar and are primarily demonstrated by a variation in the specific activity of a compound with its mole fraction in the solution. Thus, the variations in specific activity of acetone in aqueous solutions could equally well arise from failure of any of the last three assumptions. However, variations in the *ratio* of specific activities require that the relative reaction probabilities must vary with energy in order for the revised model to account for the experimental data.

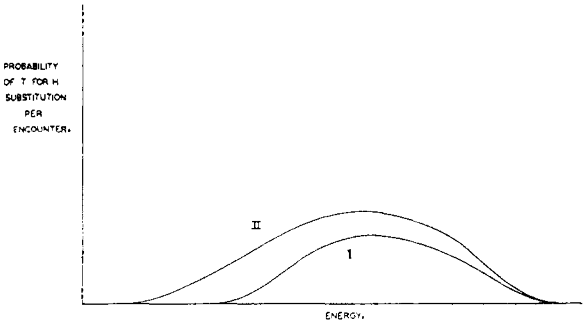
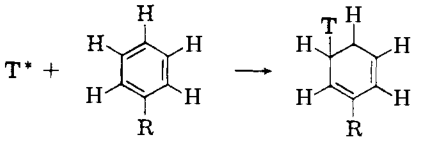


Fig. 7.—Reaction probabilities *versus* energy of recoiling atom.

Plausible reasons certainly exist for assumptions 3 and 4 not to be very accurately true. The interaction of tritium with a saturated carbon atom can scarcely last more than about 10^{-14} seconds, because of the lack of available orbitals for any longer-lived intermediate. However, a tritium atom interacting with an aromatic ring has the possibility of energetic addition to give a structure approaching



(2)

The decomposition of this radical with the elimination of tritium would then not have led to a stably bonded tritium but could have severely degraded the energy of the emerging tritium atom. The extent of the energy degradation presumably would be dependent on the actual lifetime of the intermediate in (2) (or perhaps on the similarity of the real intermediate to the free radical pictured). Tritiated cyclohexadienes are found in recoil reactions of tritium with liquid benzene[13,14] and strongly suggest that the radical of (2) does actually form in reasonable yield in such reactions.

Nevertheless, the constant specific activities of ethanol and acetone in aniline mixtures indicate that assumptions 3 and 4 correlate well with the experimental results and hence probably are quite satisfactory over the energy range in which reaction with CH_3^- and $^-CH_2^-$ positions is still possible. Any effects involving special interactions such as the cyclohexadienyl radical above must be confined largely to the lower kinetic energies below the activation energy for substitution at a saturated carbon atom.

A useful working model for competitive tritium recoil reactions (in all phases) then consists of the first four assumptions of the simple model first outline, together with relative probability variations as in Fig. 7 instead of the original assumption (5).

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tritium activity from known fluxes and cross-sections and not form actual measurement of the total activity observed. None of the measurements are more accurate than the knowledge of the actual flux during the irradiation, estimated at ±10%.

(13) A. Nesmeyanov, *et al.*, Proceedings of the I.A.E.A. Symposium on the Chemical Effects of Nuclear Transformations, Prague, 1960.

(14) J. Garland and F. S. Rowland, unpublished results.

Competitive Reactions of Cl^{38}.—A model for the behavior of competitive systems has been suggested to explain the reactions of Cl^{38} from Cl^{37} (n,γ) reactions in CCl_4–$SiCl_4$, CCl_4–cyclohexane and CCl_4–benzene systems.[15] The yield of CCl_3Cl^{38} from the former was quite consistent with simple predictions of linearity with mole fraction. However, the yields of $C_6H_{11}Cl^{38}$ and $C_6H_5Cl^{38}$ from the other two mixtures were essentially independent of mole fraction, while CCl_3Cl^{38} rose non-linearly with concentration. These yields for chlorine reactions in hydrocarbons were explained on the basis of the primary formation of an energetic complex of Cl^{38} with the hydrocarbon for all Cl^{38} atoms, with several competing modes of decomposition. From one of these, the Cl^{38} emerged degraded in energy and reacted with CCl_4 to form CCl_3Cl^{38} by atomic exchange while still above thermal energies. No such specificity in high energy interactions has yet been observed in tritium reactions. Both the geometry and the energetics of chlorine atom reactions are sufficiently unlike those of hydrogen atoms to account for such variations, but closely comparable experiments with halogens and tritium should prove very useful in elaborating on the simple model used in this paper.

(15) J. M. Miller and R. W. Dodson, *J. Chem. Phys.*, **18**, 865 (1950).

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Solvent Isotope Effects in H_2O^{16} and H_2O^{18}

BY EDWARD R. THORNTON

RECEIVED JANUARY 17, 1962

Calculated equilibrium O^{18} isotope effects involving water, hydronium ion and hydroxide ion as well as some singly-charged monatomic ions are presented. It is now possible to make rate measurements in pure H_2O^{18}. The *solvent* isotope effects should be considered in addition to possible *primary* O^{18} isotope effects.

Water containing 97% O^{18} is now available,[1] so it will be possible to measure rates in this solvent in the near future. Therefore, it is interesting to note some expected solvent isotope effects for equilibria involving transfer of ions between H_2O^{16} and H_2O^{18}. These effects should be taken into account in addition to primary isotope effects when kinetic isotope effects in the two waters are analyzed.

The calculations were performed using the vibrational transitions previously recorded for H_2O^{16} species.[2] The shifts for the O^{18} species were calculated using theoretical formulae for the normal vibrational frequencies based on a harmonic oscillator approximation. Although this approximation neglects anharmonicities, the errors in the isotope effects should be quite small because the *difference in anharmonicity* between O^{16} and O^{18} species should be very small.

Singly-charged Monatomic Ions.—The librational frequencies of the four water molecules which surround a singly-charged monatomic ion are different from the librational frequencies of water molecules in pure water, and this difference gives rise to an isotope effect. The equilibrium constants for the reaction

$$\text{ion}(4H_2O^{18}) + 4H_2O^{16} \overset{K_1}{\rightleftarrows} \text{ion}(4H_2O^{16}) + 4H_2O^{18}$$

have been calculated using the method employed by Bader[2] for H_2O *vs.* D_2O. Bader's observed librational frequencies were used for H_2O^{16}, and the shifts were calculated from the fact that they should be related inversely to the square root of the *average* moment of inertia of the molecules. The moments of inertia were calculated by assuming the H–O bond length to be 0.96 Å.[3] and the HOH angle to be 105°,[4] using the formula in Herzberg's book.[5] The resulting frequencies are listed in Table I, together with the equilibrium constants K_1. One exception which should be noted is that I^- was assumed to be *6-coördinated,*[2] not 4-coördinated.

TABLE I

CALCULATED LIBRATIONAL FREQUENCIES AND EQUILIBRIUM CONSTANTS FOR TRANSFER OF IONS BETWEEN H_2O^{18} AND H_2O^{16} AT 25°

Ion	Librational frequencies, cm.$^{-1}$		K_1
	H_2O^{16a}	H_2O^{18}	
(H_2O)	667	665.12	.....
F^-	698	696.04	0.99818
Cl^-	598	596.32	1.00448
Br^-	573	571.39	1.00611
I^{-b}	587	585.35	1.00782
Li^+	664	662.13	1.00020
Na^+	635	633.21	1.00208
K^+	625	623.24	1.00273
Rb^+	618	616.26	1.00318
Cs^+	613	611.28	1.00351

[a] Ref. 2. [b] 6-Coördinated, not 4-coördinated.

Water, Hydronium and Hydroxide Ions.—For equilibria among water, hydronium and hydroxide ions, it was necessary to take account of the internal vibrations and the translations as well as the librations. Calculations of the partition function ratios Q'/Q, where the prime refers to the O^{18} species, for H_2O, H_3O^+ and HO^- were performed, using the same frequencies and technique employed by Bader.[2] The frequencies of the O^{18} species were calculated from the O^{16} frequencies using the

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[1] YEDA Research and Development Co. Ltd., Weizmann Institute of Science, Rehovoth, Israel.

[2] R. F. W. Bader, Ph.D. Thesis in Organic Chemistry, M.I.T., 1957; C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960).

[3] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 226.

[4] G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Princeton, N. J., 1945, p. 170.

[5] Ref. 4, pp. 509 f. The principal axes were chosen by inspection.