

ABNORMAL TRITIUM ISOTOPE EFFECT IN THE ADDITION OF HYDROGEN ATOMS TO LIQUID UNSATURATED HYDROCARBONS

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INTRODUCTION

When a mixture of H and T atoms—formed by gamma radiolysis of a tritium-containing saturated hydrocarbon—is allowed to add to a dissolved olefin, among the products which are formed are the saturated hydrocarbon corresponding to the olefin, and the dimer of the radical formed in the hydrogen atom addition reaction. We have determined the isotope effect in the hydrogen atom addition reaction by measuring the specific activities of these two products and comparing these with the specific activity of the solvent saturated hydrocarbon. The isotope effects thus defined have been determined in three solvent-solute pairs: (i) tritiated cyclohexane-benzene; (ii) tritiated n-octane-cyclohexane; (iii) tritiated cyclohexane-cyclopentene. A fourth system, cyclopentane-cyclohexene, is still under study.

The initial system reflects the origin of this investigation which began with the observation of an abnormally high tritium content of the benzene polymer formed in the radiolysis of tritiated cyclohexane-benzene-¹⁴C mixtures. Such an investigation was initiated as part of our effort to determine the fate of the benzene which reacts and disappears during radiolysis of cyclohexane-benzene solutions¹.

EXPERIMENTAL TREATMENT

Materials

Cyclohexene and cyclopentene were Phillips research grade and further purified by gas chromatography. The tritium-labelled cyclohexane, cyclopentane, n-octane and carbon-14-labelled benzene were purchased from New England Nuclear Corporation and diluted to desired specific activities with the corresponding Phillips research grade hydrocarbon. All the tritium-containing hydrocarbons were further purified by gas chromatography.

Irradiations

These were carried out in a 10⁴ curie cobalt-60 radiation source (Atomic Energy of Canada; modified model 200 gamma cell). The dose rate was about 0.9 × 10²⁰ eV/g-h for liquid samples and about 1.2 × 10²⁰ eV/g-h for vapour phase samples. Liquid samples, about 1 g each, were degassed

and sealed in Pyrex ampoules and irradiated at ambient temperature of 40°. Vapour phase samples, about 0.8 g each, were contained in pre-baked 220 ml Pyrex vessels and irradiated at 100°. Total dose varied between 2.7×10^{20} eV/g and 1.8×10^{21} eV/g.

Product separation

Polymer isolation has been described elsewhere¹. Volatile products were separated by gas chromatography using Wilkens Aerograph Model A-700 or Model A-90-P. For the separation of n-octane, cyclohexane, cyclohexene, cyclopentane and cyclopentene, a 2 metre, $\frac{3}{8}$ inch O.D., column of 10 per cent silicon oil on firebrick was used in series with a 3 metre, $\frac{3}{8}$ inch O.D., column of firebrick coated with 30 per cent β, β' -oxydipropionitrile and 10 per cent silver nitrate. Depending on relative contents of the above hydrocarbon components, the chromatographic column was operated from 50–70° with carrier gas flow at about 150 ml/min. Bicyclohexyl, bicyclopentyl and other mixed dimers were separated by a 4 metre, $\frac{3}{8}$ inch O.D., 20 per cent polyester succinate column operating at 130° with carrier gas flow at 150 ml/min. Corresponding $\frac{1}{4}$ inch columns were used for analytical purposes.

Tritium specific activity analyses

Each desired product was isolated by injecting a sample of the irradiated mixture through the appropriate gas chromatographic column and collecting the separated fraction by the use of a Hamilton Collector with the U-tube containing about 0.5 ml toluene to cover the bottom of the tube, immersed in a dry ice-acetone bath. The collected toluene solution was again injected into the gas chromatograph for a repeated purification. A portion of the toluene solution, 100 μ l to 300 μ l, was then subjected to tritium analysis by liquid scintillation counting, while another portion of the same solution, 10 μ l to 50 μ l, was analysed for the product content by gas chromatography. Efficacy of the above method was verified by analyses of products, whose tritium specific activities are expected to be nearly the same as that of the solvent hydrocarbon, *e.g.* cyclohexene and bicyclohexyl from radiolysis of cyclohexane.

Radio-isotope content in polymer

The polymer isolated from each irradiated mixture of tritium-labelled cyclohexane and carbon-14 labelled benzene was subjected to carrier purification by repeated vacuum sublimation at 0° from added benzene and cyclohexane. The final residue was weighed and then redissolved in cyclohexane for simultaneous tritium and carbon-14 analysis by the dual channel technique using a Packard Tri-Carb Model 500-D Liquid Scintillation Counting System.

RESULTS

Tritiated cyclohexane-benzene-¹⁴C

The data obtained in a typical run are shown in *Table 1*. The specific

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activity of the benzene was 12,767 cpm/mg; and that of the cyclohexane was 6900 cpm/mg cyclohexane, or 48,300 cpm/mg H. The last entry in the table is simply a way of showing that more tritium is in the polybenzene

Table 1. Polymer from radiolysis of 5% benzene-¹⁴C-Cyclohexane-t mixtures (20 g of mixture irradiated)

Total weight polymer (mg)	7.05
Total ¹⁴ C (counts)	49,773
Weight benzene equivalent to radioactivity (mg)	3.90
Net weight of polycyclohexane (mg)	3.15
Tritium activity equivalent to 3.15 mg polycyclohexane	21,735
Actual total tritium (counts per minute)	78,114
Tritium in excess of polycyclohexane (counts per minute)	56,379
Specific activity of H in C ₆ H ₁₂ (counts per minute/mole H)	48,300
Tritium content of polybenzene (mmoles H/mmole C ₆ H ₆)	24

then can possibly be accounted for by simple addition of tritium atoms, and is not intended to mean more than that. *Table 2* shows the corresponding

Table 2. Tritium content of polybenzene from radiolysis of benzene-cyclohexane (t) solutions

Dose (10 ²⁰ eV/g)	Mole % benzene	Excess T in polybenzene (moles H/mole benzene)
1.93	4.7	24
4.11	4.9	24
29.38	4.9	13

result obtained at several different values of total dose; we do not know what the decrease in tritium content at the very high dose means but do not weigh this point very highly.

The high tritium content of the polybenzene fraction so calculated was not caused by an unexpected tritium enrichment in the formation of polycyclohexane, because the polymer produced from pure tritiated cyclohexane had the same specific activity as the original cyclohexane.

Tritiated n-octane-cyclohexene mixtures

The yield of cyclohexane obtained in the radiolyses of these mixtures is shown in *Table 3* (in molecules per 100 eV absorbed by the whole solution (G)).

Table 3. Formation of cyclohexane in irradiated n-octane-cyclohexene mixtures

Total dose = 4.6×10^{20} eV/g

% Cyclohexene	G (Cyclohexane)
1.2	0.35
5.7	0.82
9.3	1.1

In a run at a total dose of 2.7×10^{20} eV/g the specific tritium activity of the

cyclohexane product was found to be 1.25 $\mu\text{curies/mg H}$. The same value was found for an irradiation to a total dose of 4.5×10^{20} eV/g, demonstrating an insensitivity to total dose for this value. The specific activity of the n-octane was 3.20 $\mu\text{curies/mg H}$. It was not possible to isolate and determine the specific activity of the bicyclohexyl formed in this system because of our inability to separate the complex mixture of dimeric and intermediate products.

Tritiated cyclohexane-cyclopentene mixtures

Data obtained from these mixtures are shown in *Table 4*. The yields

Table 4. Tritium specific activity of products from radiolysis of mixtures of cyclopentene with tritiated cyclohexane^a

Phase	Mole % C ₆ H ₈	Total dose (10 ²¹ eV/g)	C ₅ H ₁₀ Activity ($\mu\text{C/mg H}$) ^b	(C ₅ H ₉) ₂ activity ^c ($\mu\text{C/mg H}$)
Liquid	0.85	1.26	0.59	0.60
Liquid	0.85	0.42	0.60	1.88 ^d
Liquid	0.85	1.26	0.67	0.71
Liquid	1.28	1.26	1.34	—
Vapour	0.85	0.12	0.23	1.65 ^d
Vapour	0.85	1.75	0.23	0.54 ^d

^a The specific activity of the cyclohexane was 3.38 $\mu\text{C/mgH}$ in all runs except 4 where it was 5.67 $\mu\text{C/mgH}$.

^b The yield of cyclopentane averaged about 0.3 molecules per 100 eV absorbed by the whole solutions; it was 2.76 in run 5.

^c The yield of bicyclopentyl averaged about 0.06 molecule per 100 eV absorbed by the whole solution.

^d Large errors in the gas chromatographic analyses make these figures uncertain.

of cyclopentane show that this is a major product, and thus that a substantial fraction of the H atoms from the cyclohexane are reacting with the olefin. The low yield of bicyclopentyl reflects the fact that the principal radical-radical reactions are between cyclopentyl and cyclohexyl radicals when the cyclopentene concentration is so low. Tritium activity was found in the unreacted cyclopentene following irradiation, demonstrating the reality of the disproportionation reaction between cyclopentyl and cyclohexyl radicals.

DISCUSSION

The cyclohexane produced in the radiolysis of tritiated n-octane-cyclohexene mixtures is enriched in tritium relative to the n-octane. If the cyclohexane contained one hydrogen atom from the n-octane, its expected specific activity would be one-twelfth that of the n-octane, neglecting isotope effects; if the cyclohexane contained two equivalent hydrogen atoms from the n-octane, the expected specific activity would be one-sixth that of the n-octane. The actual specific activity of the cyclohexane, one-third that of the n-octane, thus represents an enrichment in tritium by a factor of 2-4. The actual size of this factor would be known if the specific activity of the dimer, bicyclohexyl, could be measured since this molecule necessarily contains only one octane hydrogen atom per cyclohexyl radical, and thus

represents the tritium content of the cyclohexyl radical at the moment of birth.

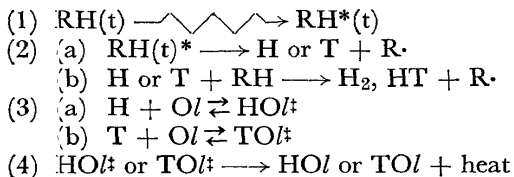
This information could not be obtained from the *n*-octane-cyclohexene mixtures, for reasons described above, but was obtained from the analogous mixture of tritiated cyclohexane with cyclopentene. Here the expected specific activity of the cyclopentane would be one-tenth that of the cyclohexane if it contained one cyclohexane hydrogen per cyclopentane molecule. The actual specific activity was one fifth that of the cyclohexane, an enrichment factor of 2. Furthermore, the specific activity of the bicyclopentyl was approximately the same as that of the cyclopentane. This demonstrates not only that the cyclopentane contained only one cyclohexane hydrogen per cyclopentane molecule, but also that the enrichment of the cyclopentane occurred only during formation of the cyclopentyl radical. No further tritium enrichment took place during the conversion of the cyclopentyl radical to cyclopentane.

With these facts in mind, the high tritium content of the benzene polymer formed in the radiolysis of the tritiated cyclohexane-benzene-¹⁴C mixtures can be assigned not only to a tritium enrichment in the addition of hydrogen and tritium atoms to the benzene, but also necessarily to the incorporation of more than one hydrogen (and tritium) atom from the cyclohexane into the benzene polymer. The number of such hydrogen atoms cannot be stated without more exact knowledge of the tritium enrichment factor.

Since the over-all reaction in the irradiated liquid cyclohexane-cyclopentene mixture consists in the transfer of hydrogen atoms from cyclohexane to cyclopentene, this tritium enrichment factor amounts to the observation that tritium atoms are transferred faster than hydrogen atoms and thus represents an abnormal isotope effect. To our knowledge, these observations are the first clearly abnormal kinetic isotope effects to be observed in a hydrogen transfer reaction. Our isotope effects have been measured by observing isotope enrichment in well defined products, not enrichment in the depleted reactant resulting from a normal isotope effect in a large side reaction, as is the case for several aromatic substitutions².

Origin of the isotope effect

We think that the origin of the abnormal isotope effect reported here can be assigned to the bond forming process in the hydrogen addition reaction. The possibility of an abnormal effect in a bond forming reaction has often been mentioned³. We can make this assignment by considering a natural reaction mechanism, shown in equations (1)–(4), and eliminating all the elementary steps except the bond forming steps, (3a) and (3b), as possible sources of tritium enrichment in the product.



The relative rates of reactions (3a) and (3b) are governed—for a

particular olefin concentration—by the relative steady state concentrations of H and T. The relative concentrations of H and T, in turn, are results of reactions forming H and T (2a), and the reverse of (3a) and (3b) and the reactions consuming H and T (2b), (3a) and (3b). Only by coincidence will the steady state concentration of H and T in the solution be the same as the concentration of H and T in the hydrocarbon, RH (t). The actual isotope effect is an over-all isotope effect for such a set of elementary processes.

Semi-quantitative statements may be made about each of the elementary processes listed above. C-H bonds are known to dissociate faster than C-T bonds, so that the concentration of H atoms resulting from reaction (2a) will be greater than the concentration of T atoms—a normal isotope effect. For a unimolecular dissociation reaction occurring at or near room temperature, and in which both stretching and bending vibrations are lost in the transition state, k_h/k_t has been calculated to have a maximum value⁴, neglecting tunnelling, of 56. Tunnelling would increase this value. However, when the species RH(t)* is an electronically excited molecule or a molecule-ion, k_h/k_d is much smaller than the calculated maximum—about 3 in CHCl₃ or CDCl₃ (ref. 5), about 1.8 in several deuterated biphenyls (ref. 6) and about 2.5–3.0 in several saturated aliphatic hydrocarbons and carbinols⁷. The ratio, k_h/k_t , would be expected to be larger than k_h/k_d by the factor⁴ $(k_h/k_d)^{1.44}$. D is known to abstract H from H₂ faster than H abstracts H from H₂, so T should react faster than H in the process (2b); this will further deplete the concentration of T relative to H in the solutions. The reverse of reaction (3a) should be faster than the reverse of reaction (3b), so that if these equilibria are important, then their result also is to deplete the solution in T relative to H. We are then left with only the bond-forming reactions as the source of tritium enrichment in the final product.

The possibility of an isotope effect in a bond-forming process depends upon the amount of vibrational energy present in the transition state of the reaction. In the order of magnitude calculations mentioned above⁴, complete loss of both bending and stretching vibrations in the transition state is assumed. This assumption means that there cannot be an isotope effect in the reverse association reaction, $H + R \rightleftharpoons [R \cdots H] \rightleftharpoons RH^\ddagger$, since no bond exists either in the initial or transition states. The existence of some retained vibrational energy in the transition state for the unimolecular dissociation is reflected in the fact that all observed isotope effects are smaller than the theoretical maximum. It may be considered as an approximation that the deviation from the maximum effect is a measure of the amount of vibrational energy in the transition state.

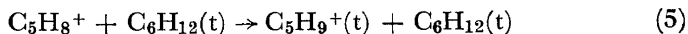
From this point of view, unimolecular dissociations with small isotope effects would be expected to indicate the possibility of large isotope effects in the reverse association reaction. It is necessary to specify the molecule which is dissociating. Existing calculations are ones which have been made for dissociation of a C-H bond in a stable molecule in thermal equilibrium with its surroundings; partition functions for such stable ground state molecules can be evaluated from known spectroscopic data. The reverse of the association reaction with which we are concerned is, however, the dissociation of a C-H bond in a highly excited radical. We cannot estimate

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partition functions either for the initial reactant nor for the transition state from existing spectroscopic data. Corresponding experimental data for isotope effects in the dissociation of such radicals—*i.e.*, C_2H_5 or C_2D_5 or $C_2H_4D \rightarrow C_2H_4$ or C_2D_4 or C_2H_3D —is also completely lacking. An additional complication is the known importance of tunnelling in hydrogen atom reactions⁸. An actual calculation of the expected abnormal isotope effect in these association reactions thus seems very difficult, even if the method of Rabinovitch⁹ can be suitably adapted.

Comparison of liquid phase results with gas phase results

The products formed by radiolysis of the tritiated cyclohexane-cyclopentene mixture in the gas phase exhibit a different phenomenon than the tritium enrichment observed in the liquid phase radiolysis (*Table 4*). In the gas phase, the hydrogen in cyclopentane has a lower specific tritium content than that of the cyclohexane—*i.e.*, a normal isotope effect is now observable. Not only has the sign of the isotope effect reversed, but since the bicyclopentyl formed in the gas phase still seems to be enriched in tritium, as it was in the liquid phase, it looks as if cyclopentane and bicyclopentyl are not both being formed entirely from the same intermediate radical. These preliminary results can be rationalized if an ion molecule reaction (or excited molecule reaction), such as reaction (5), becomes important in the gas phase in addition to the hydrogen atom reactions. Since the reaction presented in (5) is



equivalent to an ordinary hydrogen transfer reaction, a normal isotope effect might be expected—*i.e.*, H would be transferred faster than T, and the cyclopentyl species formed would be depleted in tritium compared to the cyclohexane. The difference between the tritium enrichment of the cyclopentane and the bicyclopentyl must then mean that the $C_5H_9^+$ (or its equivalent) must go to cyclopentane without going through a cyclopentyl radical stage.

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