

NOTES.

TRITIUM LABELLING OF HYDROCARBONS BY SELF-RADIATION INDUCED EXCHANGE WITH HTO.

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A convenient source of tritiated compounds utilizes the Wilzbach tritium gas exposure technique¹ which suffers from the severe disadvantage of difficulty with radiochemical purification of the parent compound². Radiation-induced exchange involving low levels (mCi/ml) of HTO with mesitylene and benzene has been reported³, however, no details of simultaneous radiation-induced degradation have been published, nor has this exchange technique been proposed as a general one-step labelling tool complementary to homogeneous⁴ and heterogeneous⁵ metal catalysis. For simplicity, T₂O exchange could be useful for tritium labelling to certain levels of activity; however, from experience with the Wilzbach technique, studies of simultaneous degradation are required before the value of the technique can be assessed.

We now wish to report for the first time the use of radio-scanning gas chromatography in a thorough study of by-product formation during HTO induced exchange with aliphatic and aromatic hydrocarbons (Table). The analytical system used consisted of a gas chromatograph, the effluent of which was directly passed into an ionization chamber mounted on a vibrating reed electrometer for simultaneous radioactivity determination. The exchange procedure simply involved adding HTO to the organic compound under vacuum in a breakseal ampoule and heating to the required temperature.

The significant features of the results (Table) are (i) all saturated and unsaturated aliphatic and aromatic hydrocarbons studied may be labelled by this simple method,

Table
Self-Radiation Induced Exchange of Organic Compounds with HTO

Parent Compound	Reaction Conditions*	Exposure Time (days)	Parent Activity (mCi/g)	% of Incorporated Activity in Parent	Principal By-product (% incorp. activity)
Cyclohexane	A	54	0.065	98	-
	B	31	0.078	98	-
	C	31	0.034	98	-
Benzene	A	54	0.10	98	1,4-cyclohexadiene (2)
	C	54	0.03	88	1,4-cyclohexadiene (12)
Toluene	A	31	0.20	98	methyl-1,4-cyclohexadiene (2)
	B	31	0.063	87	" (13)
	C	31	0.043	93	" (7)
Hexene-1	A	31	0.10	48	n-hexane (24)

- * A. Gas phase homogeneous, 110°) 0.1 ml HTO (5Ci/ml)
 B. Liquid-Liquid phase heterogeneous, 110°) 0.1 ml hydrocarbon
 C. Liquid-Liquid phase heterogeneous, Room Temp.)

(ii) no by-products were produced in detectable chemical concentration, the by-products observed being detected by virtue of their radioactivity only, thus demonstrating the remarkable value of the gas chromatograph-ion chamber assembly for this work, (iii) the radiochemical purity of the products contrasts markedly with the purities of those typical of Wilzbach tritium gas exchange where up to 70% of incorporated activity may appear as a mixture of addition and degradation products⁶, (iv) at the HTO level of activity used (5Ci/ml), the present method is valuable as a simple, one-step procedure for the tritium labelling of compounds to specific activities of $\mu\text{Ci}/\text{mmole}$, (v) the radiochemical purity of the products was better for gas phase than liquid phase systems, the principal by-product for unsaturated aliphatics and aromatics being that resulting from the addition of two hydrogen atoms to the parent compound, (vi) 1,4-cyclohexadiene is the only detectable by-product from benzene, suggesting that, mechanistically, hydrogen atom addition involving cyclohexadienyl radicals is involved; similarly, toluene yields methyl-1,4-cyclohexadiene, and (vii) hexane containing approximately 24% of the total incorporated activity is the only major by-product from n-hexane, thus confirming the preceding mechanistic conclusion and also demonstrating that with olefins, the HTO method is remarkably similar to the Wilzbach procedure where saturation of the double bond is the predominant reaction⁶.

In previous studies which may be related to the present work, HTO (mCi/ml) has been added to aromatic hydrocarbons during γ -radiolysis in order to study radiation-induced reactions at low conversions⁷. Gamma radiation has also been used to induce exchange between HTO and amides⁸.

In general, however, γ -radiolysis especially at high doses is to be avoided in tritium labelling work since this usually leads to extensive decomposition yielding results more closely resembling the Wilzbach process.

In the present work, the fact that products have been detected resulting from hydrogen addition reactions is consistent with other observations in general radiation chemistry, such as in the γ -radiolysis of benzene and mixtures where the formation of product 1,4-cyclohexadiene is accompanied by a negative isotope effect⁹. The presence of cyclohexadiene as a major by-product from benzene in the present work supports the proposal that cyclohexadienyl radical intermediates in the presence of HTO lead to labelled products³. The fact that only 1,4-cyclohexadiene and no 1,3-isomer is detected from the benzene exchange under the current experimental conditions is consistent with benzene radiolysis studies⁹ which show that the yield of the 1,4-isomer is at least tenfold higher than the 1,3-material.

The smaller degree of by-product formation in gas phase systems correlates with the observation of Garland and Rowland¹⁰ that, in the gas phase, cyclohexadienyl radicals formed by the addition of hot tritium atoms to benzene tend to decompose to benzene, while in the liquid phase, cyclohexadienes and polymeric compounds are formed. The phase result is also important since it implies that solvated electrons are not predominantly responsible for the labelling reaction. These data also show that mutual solubility of components is not critical for exchange.

In addition to the products quoted in the Table, up to 2% of "polymeric" species were formed with certain compounds. These were involatile materials with carbon numbers greater than twice that of the parent compounds and were not identified. However, these particular by-products are easily removed and do not detract from the usefulness of the technique as a simple procedure for producing clearly labelled materials of $\mu\text{Ci}/\text{mmole}$ levels of specific activity. Current work involves the use of higher specific activity tritium oxide sources to

increase the flexibility of the method, especially with respect to shortening the exposure times and determining the upper limit of attainable specific activity capable of being incorporated into compounds with a minimum of degradation.

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