

TRITIATION OF LOW MOLECULAR WEIGHT ALKANES AND ALKENES BY SELF-RADIATION INDUCED EXCHANGE WITH HTO.

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SUMMARY

The tritiation of a range of low molecular weight alkanes and alkenes has been investigated by self-radiation induced exchange with HTO at room temperature and 115°. By comparison with the Wilzbach T₂ gas exposure procedure, the HTO method yields less byproducts and radiochemical purification of the parent compound is facilitated. With alkenes, saturation of the double bond is a competing process in the HTO procedure, however the significance of this side reaction decreases with increasing temperature of exchange. The HTO technique is shown to be suitable for tritiating a wide range of hydrocarbons to medium levels of specific activity.

Key Words: Tritium, Hydrocarbon Tritiation, Radiation Exchange

INTRODUCTION

The use of high specific activity tritiated water to initiate radiation-induced exchange labelling of a number of liquid hydrocarbons has been reported in brief (1). The procedure has also been adopted advantageously for the tritiation of solids, in particular, the inositols (2). This simple tritiation procedure in which the hydrocarbon is exposed to HTO (typically 5 Ci/g) for several weeks yields products with radiochemical purities considerably higher than those typical of the conventional Wilzbach gas exposure technique (3). With compounds such as cyclohexane and toluene, radiochemical purities up to 98% were achieved and the need for rigorous purification procedures on the product was thus minimised. Some earlier studies of γ -radiation induced exchange with HTO have been reported (4) but in general such procedures lead to extensive decomposition yielding results more closely resembling the Wilzbach process.

We now report a systematic study of the tritium labelling of essentially gaseous low molecular weight hydrocarbons, both alkanes and alkenes, by exposure to HTO. The work has involved a careful analysis of the radiochemical by-products, carried out for the purposes of assessing the significance of the procedure for the tritiation of simple molecules and to permit a comparison with the results of the conventional Wilzbach method (3). Previous compounds labelled in preliminary studies (1,2) with the present HTO technique were essentially liquids and solids and labelling appeared to occur predominantly in the condensed phase as distinct from the current experiments where tritiation is in the gas phase. Such gas phase studies are important for direct comparison with equivalent Wilzbach data, since the source of tritium (T_2) in Wilzbach work is gaseous.

RESULTS AND DISCUSSION

The distribution of activity in parent compounds and byproducts for a series of alkanes labelled at room temperature is listed in Table 1 and at 115° in Table 2. In no experiment was a significant chemical yield of byproduct observed, thus no byproduct found possessed a chemical concentration greater than 1%. The experimental conditions used were such that, at the lower temperature, only about 1% of the tritium water added existed in the vapour state while, at the high temperature, the bulk of the water (70%) was in the vapour state. In each experiment all the hydrocarbon was in the vapour state, the hydrocarbon solubility in the trace of liquid water present being very slight.

The results at room temperature (Table 1) show the radiochemical purity of products (87% to 95%) to be considerably above those of the Wilzbach tritium gas procedure where typically 63% and 37% have been quoted for the radiochemical purity of methane (5) and ethane (6) respectively. At the higher temperature (115°) a significantly larger range of labelled byproducts was observed (Table 2) and these contained a much larger proportion of the incorporated activity, a trend also noted in Wilzbach and microwave labelling techniques. These byproducts were substantially those typically observed in electron or gamma radio-lysis of the respective alkanes (7).

Table 1. Labelling of alkanes at room temperature; % distribution of incorporated activity.

Product	Parent Compound *					
	Methane (% Activity)	Ethane (% Activity)	Propane (% Activity)	n-Butane (% Activity)	iso-Butane (% Activity)	
Methane	88.3	2.1	0.3	0.2	-	
Ethane	4.3	92.5	1.0	1.0	-	
Ethene	-	-	0.2	0.3	-	
Propane	3.2	-	93.4	0.4	0.8	
Propene	-	-	4.1	0.2	0.8	
n-Butane	1.0	3.8	-	94.2	-	
iso-Butane	1.0	-	-	-	94.6	
2-Methylbutane	-	1.4	-	-	-	
neo-Pentane and But-2-ene	2.2	-	-	1.2	3.8	
n-Hexane	-	0.2	-	-	-	
2-Methylpentane	-	-	1.0	-	-	
But-1-ene	-	-	-	1.7	-	
3-Methylpentane	-	-	-	0.8	-	

* Typically, activity of parent compound after 50 day exposure to HTO (0.097 ml, 5Ci/ml) at room temperature was 50 μ Ci, i.e. 20 mCi/mole.

For comparison purposes, typical Wilzbach product distributions are (5,6):
 for methane: CH_4 63%, C_2H_6 28%, C_3H_8 5%, n- C_4H_{10} 2.2%, i- C_4H_{10} 2.2%
 for ethane: C_2H_6 37%, C_3H_8 41%, C_4H_{10} 22%

Table 2. Labelling of alkanes at 115°C; % distribution of incorporated activity.

Product	Parent Compound*				
	Methane (% Activity)	Ethane (% Activity)	Propane (% Activity)	n-Butane (% Activity)	iso-Butane (% Activity)
Methane	41.6	4.8	12	4.3	0.6
Ethane	15	45.1	11	8.7	0.4
Ethene	-	-	1.9	4.4	-
Propane	11	7.6	48.2	5.1	13
Propene	-	1.3	6.0	2.0	0.8
n-Butane	3.2	21	1.5	60.3	-
iso-Butane	5.6	2.0	2.7	-	57.6
n-Pentane	0.4	1.7	0.9	0.4	-
2-Methylbutane	3.4	2.1	7.5	1.5	1.2
neo-Pentane/ But-2-ene	13	0.9	0.5	3.1	26
But-1-ene	-	1.3	-	2.4	-
cis-But-2-ene	-	0.5	-	1.3	-
2,2-Dimethylbutane/ trans-Pent-2-ene	6.8	-	0.2	-	0.2
3-Methylpentane	-	7.3	1.8	6.3	0.1
n-Hexane	-	4.4	0.5	0.2	-
2-Methylpentane	-	-	3.3	-	0.1
2,3-Dimethylpentane	-	-	2.0	-	-

* Typically, activity of parent compound after 50 day exposure to HTO (0.097 ml, 5 Ci/ml) at 115°C was 80 µCi, i.e. 30 mCi/mole.

With methane or ethane, the principal active byproduct found was that resulting from a dimerization reaction to yield ethane and butane respectively. With the longer chain alkanes degradation products became more significant and interaction of these degraded species and the parent molecule led to a variety of higher molecular weight byproducts. The radiochemical purity of the product increased with the carbon chain length of hydrocarbon and, at room temperature, the radiochemical purity of 95% for *n*-butane and *iso*-butane was close to that observed previously for cyclohexane and toluene (1). It thus appears that the activity distribution between parent and byproducts is independent of skeletal structure of parent i.e. whether the hydrocarbon is straight, branched, cyclic or aromatic.

By contrast, the results for the two alkenes studied, ethene and propene (Table 3), show clearly that saturation of the alkene to the corresponding labelled alkane accompanies the labelling of the parent compound and lower radiochemical purity for such molecules is typical as observed previously for hexene(1). The degree of saturation of the parent molecule appeared to be significantly lower at the higher temperature, particularly with propene.

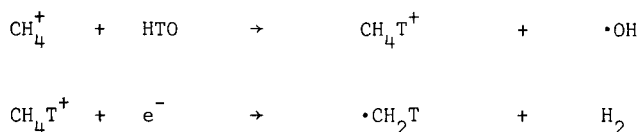
While the present studies were not designed to elucidate the mechanism of the tritiation reactions, it is significant mechanistically that the formation of labelled byproducts in the tritiation of alkanes was markedly higher at the elevated temperature when the HTO concentration in the gas phase was some 70 times above that at ambient temperatures. Since a very small fraction of the hydrocarbon present was dissolved in the liquid phase (10^{-6}), it is likely that gas phase reactions were alone responsible for the products observed.

Thus, if the generally accepted mechanisms operable in the radiolysis of methane are assumed, then labelled methane may be presumed to result from interaction of $\cdot\text{CH}_3$ with HTO, while the interaction of $\cdot\text{CH}_3$ with organic species would yield predominantly unlabelled stable products. However, at high HTO concentrations the initial ionic species, such as CH_4^+ , may interact with HTO, in successful competition with its normal interaction with CH_4 , to yield CH_5^+ .

Table 3. Labelling of alkenes with HTO; % distribution of incorporated activity*

Product	Ethene		Product	Propene	
	Room Temp. (% Activity)	115°C. (% Activity)		Room Temp. (% Activity)	115°C. (% Activity)
Methane	2.1	0.5	Propane	45	5.6
Ethane	41.4	8.8	Propene	43	49
Ethene	22	25	2-Methylbutane	-	4.1
Ethyne	2.2	36.3	2,2-dimethylbutane/ Pent-2-ene	1	2.9
<u>n</u> -Butane	24	6.0	2-Methylpentane	6	6.4
But-1-ene	2.3	2.3	Other products	5	32
neo-Pentane/ But-2-ene	-	2.7			
2,2-dimethylbutane/ <u>trans</u> -Pent-2-ene	-	1.2			
<u>cis</u> -Pent-2-ene	-	1.1			
<u>trans</u> -Hex-2-ene	-	2.9			
<u>cis</u> -Hex-2-ene	-	3.2			
Other products	6	10			

*Total activity of listed products after 50 day exposure to HTO (0.097 ml, 5 Ci/ml) was typically 70 μ Ci after room temperature exposure, 120 μ Ci after 115°C exposure. Quantity of parent 2.8×10^{-3} moles.



Labelled byproducts would then result from the usual labelled methyl radical reactions with organic species. From the relatively low yield of tritiated byproducts obtained from methane when the gas phase HTO pressure was low, as occurred in the ambient temperature experiments, it appears that ion-molecule reactions of the above type to form tritiated intermediates were relatively unimportant under those conditions.

In addition to reactions initiated by irradiation of the organic component, some part of the radiation energy would be deposited within the gas phase water component of the system leading to the formation of the several reactive intermediates present in radiolysed water vapour. At the higher water concentration these processes are likely to have been significant and may have led to the formation of labelled parent, by reactions such as hot atom displacement by T \cdot , as well as a variety of other labelled products.

Earlier work with inositols (2) suggested that some similarity may exist between HTO labelling systems and the processes observed in negative ion mass spectrometry where de-energised primary electrons are readily captured in a low energy process to give relatively stable anions. It is thus plausible to suggest that negative ion intermediates may also be just as important in the present HTO labelling mechanisms as are positive ions and radicals.

In the Wilzbach T₂ gas phase system a "tritium recoil" path was thought to be responsible for the production of part of the labelled products (8). In the present HTO system such a path is not possible since decay of the tritium atom in HTO yields a non-tritiated recoil species. This may account for at least part of the difference between the Wilzbach and HTO results.

Finally, the present data illustrate the possibilities of using the HTO technique as a general tritium labelling tool for hydrocarbons. The results show that simple alkanes may be labelled with radiochemical purities considerably

higher than those typical of the conventional Wilzbach gas exposure technique, particularly where ambient temperature conditions are chosen and the hydrocarbon pressure considerably exceeds the HTO vapour pressure. Although rates of tritium incorporation are relatively slow in the present HTO technique, byproduct formation is not excessive and does not generally preclude radiochemical purification of the labelled parent. The experimental simplicity of the HTO technique renders it attractive as a labelling procedure and an assessment of its usefulness with more complex molecules is continuing.

EXPERIMENTAL

Hydrocarbon gases (67.8 ml at 760 mm) were condensed into a reaction vial (47.1 ml) followed by high specific activity tritiated water (0.097 ml, 5 Ci/g), the reaction vial sealed, and the mixture held either at room temperature or heated to 115°C for the required time. At the end of the exposure period the bulk of the hydrocarbon was distilled from the reaction vial through a break seal and sampled for analysis on a gas liquid chromatograph coupled to a proportional counter. Traces of high molecular weight by-products may have remained in the reaction flask and been excluded from the analysis.

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