

The Recoil Tritium Labelling Reaction as a Function of Tritium Energy and Molecular Size

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ABSTRACT

Hydrocarbons can easily be labelled by recoil tritium atoms. Near the end of the recoil track, after the triton has been neutralised and whilst it still retains some excess translational energy, a tritium atom can replace hydrogen atoms in C-H bonds with high collision efficiency. Results of studies on this reaction in hydrocarbons (ethylene, ethane, propylene, butane, n-pentane and trans-butene-2) are analysed using the Estrup-Wolfgang method. It is found that the reactivity integral (I) for the labelling reaction increases with the size of the molecule labelled and that it is usually larger for an alkene than for the corresponding alkane. Furthermore, it is shown that the labelling reaction commences at relatively higher tritium atom energies as the size of the molecule is increased. The implications of these results for the formation of tracer amounts of tritium labelled hydrocarbons are discussed.

INTRODUCTION

The nuclear reaction ${}^3\text{He} (n, p){}^3\text{H}$ gives a recoil triton of energy 0.2 MeV. After dissipation of excess energy the neutral tritium reacts with hydrocarbons in an energy range of around 2-20 eV. A variety of labelled compounds are formed, but 90 % of the tritium that reacts can be accounted for by two main reactions. These are direct hydrogen displacement to give the tritium labelled hydrocarbon and hydrogen abstraction to give HT. The latter reaction is also observed with thermal tritium. In the case of alkenes an addition reaction to the double bond also occurs ⁽¹⁾.

A large number of hydrocarbon systems have been studied by utilising recoil tritium in this way ^(1, 2). A general kinetic theory ⁽²⁾ permits three

parameters to be evaluated. α , the average logarithmic energy loss ($\alpha = \ln$ energy before collision/energy after collision), I , the reactivity integral

$$I = \int_{E_1}^{E_2} \frac{p(E)}{E} dE,$$

$E_2 - E_1$ the energy range for hot reaction, $p(E)$ probability of atom, energy E , reacting upon collision, and K_i , the "energy shadowing integral"

$$K_i = \int_{E_1}^{E_2} \frac{p_i(E)}{E} \left[\int_E^{E_2} \frac{p(E)}{E} dE \right] dE$$

$E_2 - E_1$ is the energy range for formation of product i , $p_i(E)$ is probability of atom, energy E , reacting to form product i .

These parameters are found experimentally by observing the total yield of recoil tritium found as labelled product in a series of tubes in which the hydrocarbon : inert gas (helium-4) is altered. The alteration of this ratio effectively changes the tritium energy spectrum in the chemical reaction range (~ 2 -20 eV). Oxygen (~ 2 cm Hg) is used to scavenge thermal tritium and radicals.

EXPERIMENTAL

Quartz ampoules of 2 cm diameter and about 16-20 cm³ capacity were flamed out whilst under vacuum and filled with the required amounts of hydrocarbon, helium-3, oxygen and helium-4, in that order, whilst immersed in liquid nitrogen. The samples were sealed off at a constriction just above the surface of the liquid nitrogen. The total pressure at room temperature in the samples was usually about one atmosphere. Hydrocarbons of high purity were obtained from the National Chemical Laboratory, England, and used directly. Helium-3 of high purity was purchased from the Mound Laboratory, (Monsanto Ltd.), Miamisberg, Ohio, U. S. A. The remaining traces of impurity were removed with a nickel getter^(3, 4).

Neutron irradiations were carried out at the U. K. A. W. R. E. HERALD reactor (Aldermaston) ($\sim 10^{10}$ n, cm⁻² sec⁻¹). In a typical sample containing about 2 cm Hg of helium-3 this produces about 8×10^{13} tritons with an activity of about 10^5 d.p.s. Since such a sample contains about 10^{20} molecules and the energy of the nuclear reaction that produces each triton is 0.8 Mev, about 6×10^{-2} e.v. per molecule is deposited throughout the sample. No gross radiation damage (i.e. $\nless 1$ %) was detected in the control chromatographic mass trace.

The integrated neutron dose received by the samples was measured by cobalt monitor wires placed amongst the ampoules. The fast neutron dose (determined by sulphur pellets) was less than 1 % of the thermal dose. The total gamma dose received by each sample was about 10^4 rads. Simple cal-

culations show that the major source of radiation damage is due to recoiling protons and tritons.

The products were analysed by gas-phase chromatography and flow proportional counting⁽⁵⁾. G. L. C. columns were a 4 ft silica gel (HT/methane), 13 ft 704 silicone oil on firebrick (30 % w/w) and dimethylformamide on firebrick (13 ft — 30 % w/w, operated at 0° C).

The electronic counting equipment used was of the I. D. L. 1 800 series with a determined overall efficiency of 82 ± 3 %⁶.

KINETIC THEORY AND I VALUES.

The use of moderators permits the probability that a hot atom will have a particular energy E , $n(E)$, to be varied. The Estrup-Wolfgang kinetic theory of hot reactions^(7, 8) permits the total probability of a T atom engaging in any hot reaction, P , to be expressed in terms of the moderating powers (α 's) and collision probabilities (f 's) of the various components. For a single reactant (R) and an inert moderator (M)

$$-[\ln(1-P)]^{-1} = \frac{\alpha(R)}{I} + \frac{\alpha(M)}{I} \frac{f_M}{f_R} \quad (1)$$

If *all* the hot reaction products are observed then $\alpha(R)$ and I can be expressed in terms of $\alpha(M)$. A graph of $-\ln(1-P)^{-1}$ versus f_M/f_R should be a straight line of slope $\alpha(M)/I$ and intercept $\alpha(R)/I$. Using $\alpha(R)$ it is possible to extend the kinetic theory to describe the yields of individual labelled products

$$P_i = (f/\alpha)I_i - (f/\alpha)^2K_i + (f/\alpha)^3L_i - (f/\alpha)^4M_i \dots \quad (2)$$

The terms K_i , L_i , etc. allow for the possibility that the hot T atom has reacted at an energy above the range of formation of i and consequently removed from the systems. In most cases (except production of HT) the terms in L_i , M_i , etc. are insignificant.

Plots of equations (1) and (2) are shown for ethylene in Figures 1 and 2 respectively. All hydrocarbons studied gave similar plots.

Table 1 shows the values of (R) , I_{Total} and I_{parent} found. All values are in units of $\alpha_{\text{Helium-4}}$.

TABLE 1.

System (all He ₄ moderated)	α	I_{Total}	I_{parent}
Ethylene	3.3	2.75	1.64
Ethane	3.04	2.30	0.57
Propylene	4.0	3.25	1.06
Trans-butene-2	5.0	4.40	0.75
Butane	4.5	3.34	0.77
<i>n</i> -pentane	5.9	4.38	1.05

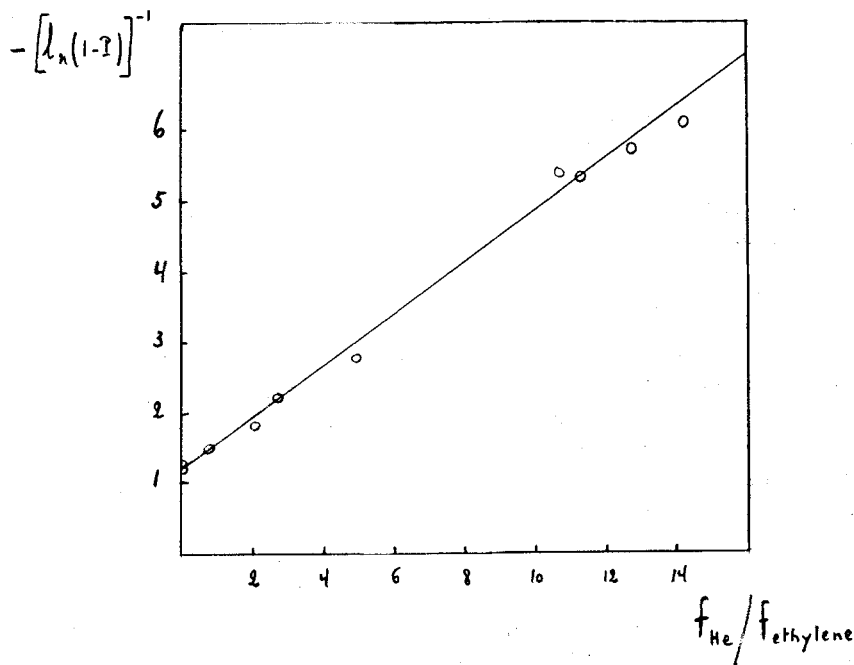
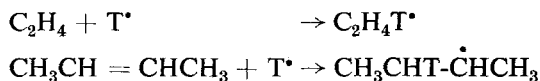


FIG. 1. Graph from equation (1) for ethylene.

The value of I_{Total} , I_{parent} and α all increase with increasing size of reactant molecule for alkanes. This suggests a connection between size and ability to absorb the excess translational energy of the tritium atom. Figure 3 shows that a rough correlation may be obtained between the number of degrees of vibrational freedom and α both for alkanes and alkenes. Alpha values for alkenes are greater than those of the corresponding alkanes — this is probably due to the π electron cloud absorbing some of the excess energy.

The I_{parent} values of alkenes in the homologous series ethylene, propylene and butene decrease and this would appear to contradict the above idea developed for alkanes.

However, whereas labelled alkane parent can only be formed by direct hydrogen displacement, alkenes can undergo an addition reaction at the double bond⁽⁹⁾ to form an excited radical which follows the normal unimolecular decomposition modes.



With the excited butyl radical, the weakest C-C bond is broken forming labelled propylene and a methyl radical. However, in the case of ethylene

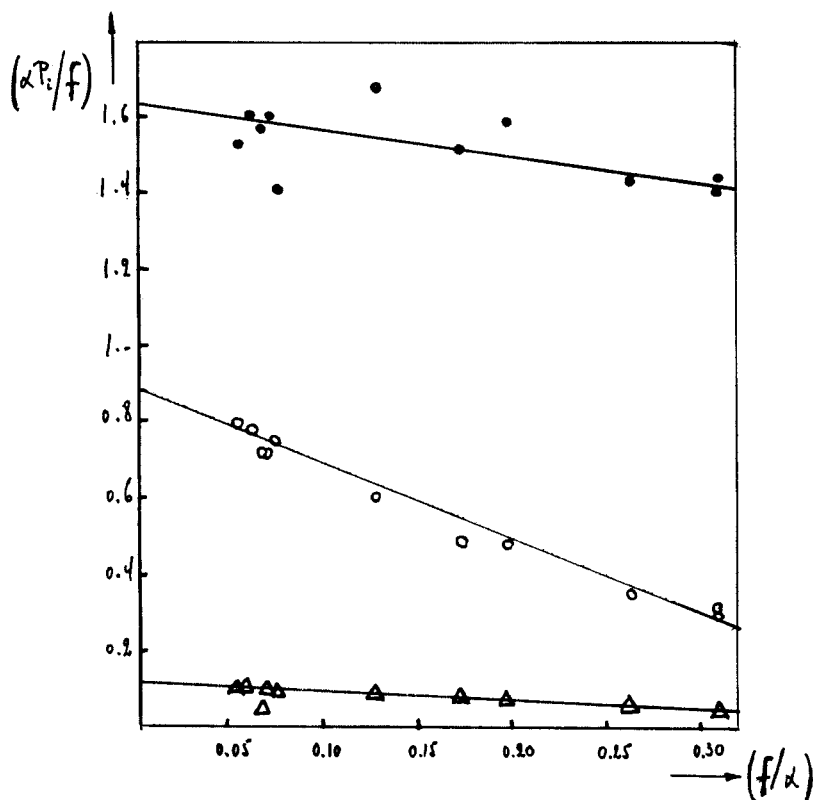


FIG. 2. Graph from equation (2) for individual products from ethylene.

- C₂H₃T
- HT
- △ C₂HT

only a C-H bond can be broken in which case labelled parent molecule is formed.

It is the labelled ethylene formed by this addition reaction which increases I_{parent} .

This is further illustrated by 1:3 butadiene, the I_{parent} value of 1.91 being much larger than I_{parent} of trans-butene-2 (0.75)⁴.

K INTEGRALS

These integrals have been called "energy shadowing" integrals⁽⁸⁾. It is possible to evaluate theoretical maximum and minimum values of K_i and compare them with experimental K_i values. It has been shown^(4, 10) that the maximum value of K_i is $(1/2)I_i^2 + I_i I_{\text{rest}}$ and the minimum value is $(1/2)I_i^2$.

Table 2 shows typical values, in this case ethylene.

TABLE 2.

Product	I_i	K_i	K_{\min}	K_{\max}
HT	0.89	1.97	0.395	1.96
C_2H_3T	1.64	0.70	1.34	2.99
C_2HT	0.12	0.23	0.009	0.313

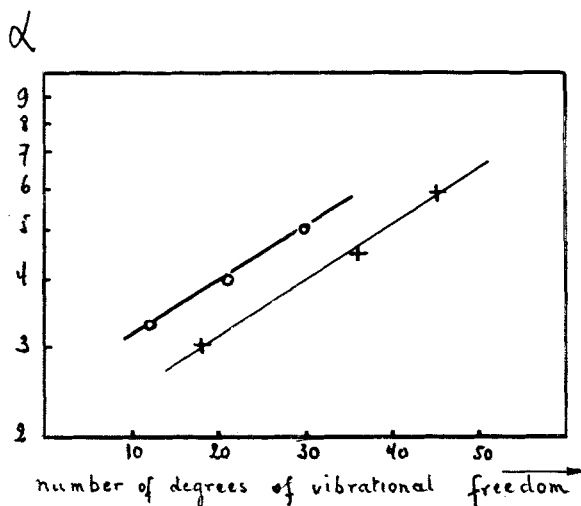


FIG. 3. Correlation between the number of degrees of vibrational freedom and α values for alkanes and alkenes.

○ alkenes
+ alkanes

The fact that the value of K_{HT} approaches the K_{\max} value indicates that the formation of HT is "shadowed" a lot by the other reactions. Qualitatively this shows that HT is formed at the low end of the energy spectrum. Also as K_{parent} approaches and in fact is lower than K_{\min} , this reaction must proceed with the very "hottest" T atoms.

The general trends shown by ethylene are apparent in all the systems studied^(4, 10), i.e. the parent labelling reaction occurs at high energies (~ 10 -20 eV) whereas the hydrogen abstraction reaction takes place at the lowest energies.

APPLICATION TO MIXTURES

The kinetic theory in an adapted form⁽⁴⁾ can also be applied to mixtures to obtain values of K_A and K_B where A and B represent the reactant species.

Table 3 shows the results obtained from ethylene and trans-butene-2 mixtures.

TABLE 3.

	K_t	$K_A(i)$	I_t	I_A
Ethylene	0.70	1.80	1.64	1.70
Trans-butene-2	0.55	-0.50	0.75	0.64

K_t is the value obtained from single reactant studies.

I_A are the values obtained in the mixture studies.

As would be expected from the kinetic theory for moderated mixtures the values of $I_{p.rent}$ obtained are, within experimental error, the same as those obtained from single reactant studies. However, the value of K for ethylene has increased drastically, whereas K for trans-butene-2 has increased only slightly. Qualitatively this shows that the trans-butene-2 labelling reaction occurs at a higher energy than that of ethylene, as ethylene suffers a lot more shadowing than does butene in the mixture.

RESULTS

It appears that the energy at which recoil tritium atoms can react to form stable chemical products with a hydrocarbon increases with increasing size of the molecule and that the labelling reaction occurs at the high energy end of the reactivity spectrum.

It is also observed that the I integrals increase with increasing molecular size. However, since α also increases hot atoms are more efficiently moderated by larger molecules. Thus, although probability of reaction upon collision increases, the probability of collision decreases. Thus the observed hot yield and also I/α are found to be remarkably constant within a homologous series of hydrocarbons.

The reactivity integrals obtained for butene-2 and butane enable a tentative comparison of reactivity of sp^2 and sp^3 CH sites to be made. If it is assumed that the reactivity and probability of being struck are the same for all hydrogens in butane and for the CH_3 groups in butene-2 then the portion of the reactivity integral relating to an sp^2 C-H bond is $0.5 (0.75 - (0.77 \times 6) / 10) = 0.145$, just about double the corresponding value for a sp^3 C-H site (0.077). That olefinic sites are more reactive than paraffinic has already been suggested by the work of Nesmeyanov *et al* on cyclohexene⁽¹¹⁾.

The increased reactivity of sp^2 sites makes molecules such as ethylene or 1 : 3 butadiene the most suitable candidates for tritium labelling by the

recoil method. About 40 % of the tritium atoms available for hot reactions form labelled ethylene but only 24 % form labelled ethane.

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