The Formation of Excited Ethane in the Tritium Recoil Labelling Reaction

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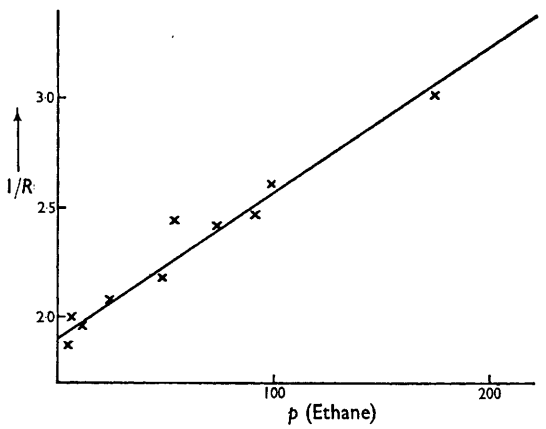
RECOIL tritium atoms [$^3He(n,p)T$] can react with gaseous hydrocarbons by hydrogen replacement; labelled radicals are also formed.[1] Wolfgang *et al.*[2] have suggested that such radicals may be formed by a unique hot reaction in which two groups are simultaneously displaced (double-knock) whilst Rowland[3] believes them to originate from the decomposition of a molecule excited by the labelling process.

The reaction of recoil tritium atoms with ethane was studied[4] in the presence of bromine scavenger using different pressures of ethane, bromine, and helium-3 (see Table). In all cases the total neutron dose was $(1{\cdot}05 \pm 0{\cdot}05) \times 10^{15}$ *n* cm.$^{-2}$ and analyses were delayed until the bromine activity was negligible. In a series of four tubes (B), in which the ethane-to-bromine ratio was held approximately constant and in which, therefore, the hot tritium atoms' energy distribution was also approximately constant,[5] it was found that *R* [= (activity in CH_2TBr)/(activity in C_2H_5T)] was *not* constant. This shows that CH_2T· (assumed precursor of CH_2TBr) was not formed by a "double-knock" hot reaction. A comparison of tubes with similar ethane pressures shows that *R* is insensitive to changes in bromine pressure. Thus the formation of CH_2TBr from a reaction between C_2H_5T (excited) and bromine may be discounted.

Further this result shows, since bromine also acts as a moderator,[5] that CH_2TBr and C_2H_5T are both formed from tritium atoms of similar energies. All these observations are consistent with CH_2T. radicals being formed from the unimolecular decomposition of excited C_2H_5T.



FIGURE

TABLE

Tube number	B2	B3	T19	M34	T22	B4	T21	T23	B7	T24
Tube contents[a]:—										
C_2H_6	173·8	98·5	91·0	73·7	53·9	48·2	23·9	11·0	6·76	4·33
Br_2	11·8	6·7	2·1	7·0	22·1	2·9	35·4	36·3	0·8	33·1
^3He	9·7	10·2	2·4	2·7	2·0	10·3	2·1	2·4	9·6	2·3
R	0·331	0·384	0·405	0·414	0·410	0·458	0·480	0·510	0·500	0·535

[a] all pressure in cm. Hg.

To analyse the results it is necessary to assume that only a fraction f_2 of the labelled ethane molecules have enough energy of excitation (E^*) to

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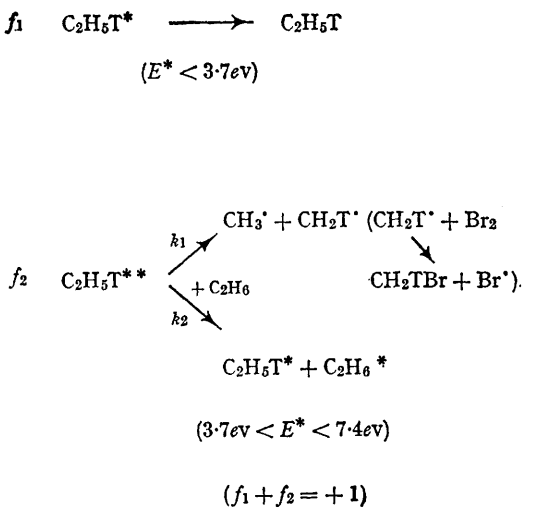
have the chance of unimolecular decomposition, thus, [since D (C–C) ethane = 3·7 *ev*],



Then $(R)^{-1} = f_1/f_2 + (k_2/k_1f_2)\ p$, where p is pressure of ethane.

The straight line in the Figure indicates accord with the proposed kinetic scheme. 65·5% (= $100f_1$) of the labelled ethane molecules do not have the excitation energy ever to undergo a unimolecular decomposition. For the other 34·5%, (k_1/k_2) = 433 cms. Following Marcus[6] and assuming the bimolecular rate constant to be $Z\lambda$, and taking Z to be 5×10^7 cm.$^{-1}$ sec.$^{-1}$, than $k_1 = 2{\cdot}17 \times 10^{10}\lambda$ sec.$^{-1}$, which corresponds to an average half-life for excited C_2H_5T of 32 $\mu\mu$ secs. and $E^* \sim 5$ *ev* if λ (the efficiency of the deactivating collison) = + 1. Since it seems unreasonable to suppose that all the $C_2H_5T^{**}$ molecules will have the same E^* and since for each E^* there will be a corresponding value of k_1/k_2, these results represent values averaged over all the excited molecules.

(*Received, February 7th*, 1966; *Com.* 079.)

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