

A Five-centre Transition Complex involving $\cdot\text{N}_2\text{T}$

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Summary The enhanced yield of labelled propylene observed when recoil tritium reacts with *trans*-but-2-ene in the presence of nitrogen is explained by postulating an excited $\cdot\text{N}=\text{NT}$ which can react with the olefin through a five-centre transition complex to form $[\text{C}_4\text{H}_8\text{T}]^{\cdot*}$ and nitrogen and which decomposes in the usual way to form propylene.

RECOIL tritium atoms produced by $^3\text{He}(n,p)^3\text{H}$ can react by addition to olefins whilst they are translationally excited, *i.e.* 'hot'. An excited radical is formed which decomposes to a labelled olefin and a smaller radical.¹ A comparison of the yields of labelled propylene formed from *trans*-but-2-ene in the presence of increasing amounts of helium, oxygen, or nitrogen shows that the yield of propylene is enhanced by moderate amounts of nitrogen. The experimental results are presented in Figure 1. The yield of propylene is given as a *P* value,^{2,3} *i.e.* the fraction of the tritium available for hot reaction that is found as labelled propylene. The concentration of but-2-ene is corrected for the different collision sizes of the components. These cross-sections (S_j for component *j*) for collisions with a tritium atom were estimated from viscosity data,⁴ [He , 20.35; O_2 , 27.40; N_2 , 30.0; *trans*-but-2-ene, 42.20; (\AA)²]. The size corrected concentration of *trans*-but-2-ene is $f(\text{but}) = S(\text{but}) \cdot X(\text{but}) / \sum S_j X_j$, where X_j is concentration in g mol^{-1} of *j*. In order to compare directly the results from systems moderated by helium, oxygen, and nitrogen the relative moderating powers of these molecules must be estimated. This can be done by an Estrup-Wolfgang² "first-kind" analysis of the data in which $[-\ln\{1 - P(\text{all hot products})\}]^{-1}$ is plotted against

$[1 - f(\text{but})]/f(\text{but})$. The ratio $\alpha(\text{hydrocarbon})/\alpha(\text{moderator})$ is obtained from this analysis; α is the mean logarithmic energy loss parameter, see equation (1).

$$\alpha = \left\langle \ln \left(\frac{\text{energy before collision}}{\text{energy after collision}} \right) \right\rangle \text{average} \quad (1)$$

Experimentally determined values⁵ are $\alpha(\text{but})/\alpha(\text{He}) = 4.4$, $\alpha(\text{but})/\alpha(\text{O}_2) = 3.8$, and $\alpha(\text{but})/\alpha(\text{N}_2) = 3.9$. The actual value of α for any particular sample can be estimated from

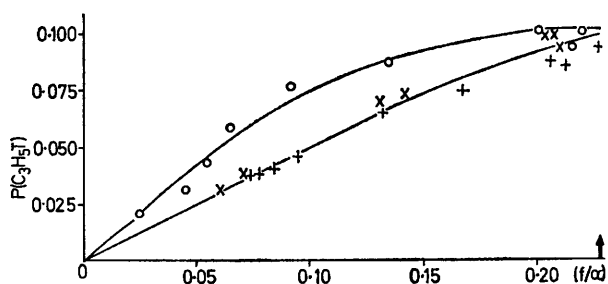


FIGURE 1. Yield of $[\text{}^3\text{H}]$ propylene from the reaction of recoil tritium atoms with *trans*-but-2-ene in the presence of helium (+), oxygen (x) or nitrogen (O). The fraction of tritium, available for reaction, found as propylene is indicated on the vertical axis. The horizontal axis is in units of $f(\alpha)$, see text. Arrow indicates pure *trans*-but-2-ene.

$\alpha = \sum f_j \alpha_j$, it is usually expressed in terms of $\alpha(\text{moderator})$. For a direct comparison of results using the three different moderators the values of α have all been presented in terms

of $\alpha(\text{He})$. The horizontal axis in Figure 1 is in units of $f(\text{but})/[\alpha(\text{but})/\alpha(\text{He})]$.

As can be seen, the propylene yields, when helium or oxygen is added, behave in a simple and identical way. Deviations from this line are observed when nitrogen is added, and are greatest at approximately equimolar amounts of but-2-ene and nitrogen. This suggests a bimolecular process in which nitrogen and but-2-ene act in concert to produce propylene.

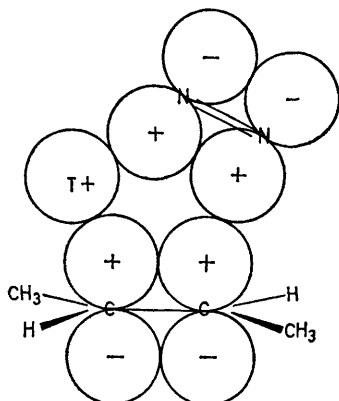


FIGURE 2

There seems no reason why hot tritium atoms should not react with nitrogen to produce $[\cdot\text{N}=\text{N}-\text{T}]$. By analogy with addition to a carbon-carbon double bond¹ one would expect most of these $\cdot\text{N}_2\text{T}$ radicals to be vibrationally excited. If $\cdot\text{N}_2\text{T}^*$ radicals were to collide with but-2-ene addition might take place to form, $[\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}(\text{N}=\text{NT})\cdot\text{CH}_3]^*$. A consideration of the structure and orbital availability (Figure 2) in such a radical leads one to expect that

it would be able to rearrange rapidly to a $[\text{}^3\text{H}_2]\text{S}$ -butyl radical and nitrogen. This is because the cyclic in-phase interaction of five orbitals is involved.^{6,7} The system is analogous to the π orbital system of the cyclopentadienyl radical, with three bonding orbitals. Five electrons can therefore be accommodated in stable orbitals at all stages of the reaction; thus the activation energy for the proposed reaction, $[\text{CH}_3\cdot\dot{\text{C}}\text{H}\cdot\text{CH}(\text{N}=\text{NT})\cdot\text{CH}_3]^* \rightarrow [\text{CH}_3\cdot\text{C}\dot{\text{H}}\text{T}\cdot\dot{\text{C}}\text{H}\cdot\text{CH}_3]^* + \text{N}_2$ will be low. (The process is in contradistinction to the cyclic in-phase interaction of only *four* orbitals which must pass through a structure with only one bonding orbital—cyclobutadiene type—and which is therefore associated with a high activation energy).

The result of this process is to form an excited $[\text{}^3\text{H}]\text{S}$ -butyl radical, as if the nitrogen had not intervened. This radical then decomposes to propylene in the usual way. The nitrogen in this special case acts as a "carrier" for the hot tritium atom. The bimolecular character of the reaction can also be understood by this mechanism. In the presence of excess nitrogen the vibrational excitation of $\cdot\text{N}_2\text{T}^*$ is degraded before it can react with but-2-ene; either the reaction does not take place, or more likely, a non-excited $[\text{}^3\text{H}]\text{S}$ -butyl radical is formed which does not decompose. Collisions with helium or oxygen do not give rise to this special reaction. Helium can only remove excess energy translationally upon collision with hot tritium, and oxygen cannot act in the same way as nitrogen because the activation energy for addition is so low. Hot tritium would merely form $[\cdot\text{O}_2\text{T}]^{**}$ which would decompose rapidly.

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