The Kinetics of the *cis–trans*-Isomerisation of the 1-Methylallyl Radical. A New Technique for the Study of Unimolecular Radical Reactions

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Summary A rate constant for the *cis–trans*-isomerisation of the 1-methylallyl radical is obtained from a study of the competition between radical isomerisation and trapping with HI.

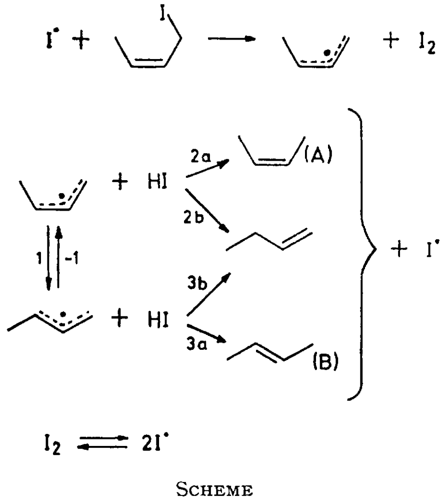
In the previous communication,[1] we argued that the addition of HI to dienes is a six-centre molecular process. The geometric requirements of this cyclic transition state mean that the initial product of addition to butadiene is *cis*-1-iodobut-2-ene. However, this iodide, like other allylic iodides,[2] is unstable in the presence of HI and reacts further to form butenes and I_2.[3] If this process follows the usual iodine atom chain,[4] it will involve the steps shown in the Scheme. The significant feature of this mechanism is that the precursor iodide and therefore the initially formed 1-methylallyl radical are both in the *cis* form. If radical isomerisation (step 1) does not compete effectively with trapping by HI (step 2) then the but-2-ene product should be predominantly *cis*.

We report here a test of this prediction, and some further results on the isomerisation of *cis*-1-methylallyl radical, obtained from an examination of the butene distribution in the low temperature reaction of HI with butadiene. Our apparatus is similar to one already described.[5] HI reaction pressures were limited to < 50 torr† to avoid condensation during sampling. Checks were made to ensure that no reaction occurred during sampling and prior to analysis (by g.l.c.). In a preliminary experiment at 60 ± 5° ($[CH_2{=}CH{-}CH{=}CH_2]$ = 104 torr, [HI] = 11 torr), *ca.* 0·8% of butenes were formed in five hours. A value of 6·7 was obtained for the ratio [*cis*-but-2-ene]/[*trans*-but-2-ene].

In order to test the mechanism further we have investigated the effect of variation of [HI]. A stationary-state treatment of steps 1, 2, and 3 yields the expression (1).

$$\frac{d[A]}{d[B]} = \frac{k_{2a}}{k_{3a}}\left(\frac{k_{-1}}{k_1} + \frac{k_{3a} + k_{3b}}{k_1}[HI]\right) \qquad (1)$$

The Figure shows the results of a series of experiments at 89·8 ± 0·5°, carried to < 10% conversion,‡ in which equation (1) was tested. Within experimental error a linear fit is obtained (with slope 0·0259 ± 0·0023 torr^{-1} and intercept 0·96 ∓ 0·08) when the butadiene pressure is held



Scheme

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† 1 torr = 133 N m^{-2}.

‡ Separate experiments showed that the butene distribution did not vary in this range. The I_2 catalysed isomerisation of the butenes[9] requires higher temperatures.

constant at 10 torr. If the butadiene pressure is increased or nitrogen added, the *cis/trans* ratio falls below the line. These effects are to be expected if step 1 is a unimolecular reaction not at its high pressure limit, although a slight curvature in the plot should also occur.

These results lend support to the suggested mechanism and yield the following information:

$$\frac{k_{2a}}{k_{3a}} \times \frac{k_{-1}}{k_1} = 0{\cdot}96 \text{ and } \frac{k_{-1}}{k_{3a} + k_{3b}} = 37{\cdot}1 \pm 6{\cdot}3 \text{ torr} = 10^{-2{\cdot}79} \text{ mol l}^{-1}$$

If the reactivities of the terminal positions of both isomers of the radical are the same then the equilibrium constant (= [*trans*]/[*cis*]) = 1·04 ± 0·08. An estimate of $k_{3a} + k_{3b}$ (*ca.* $10^{7{\cdot}5}$ l mol^{-1} s^{-1}) may be made from the reverse reaction rate constants and assumed thermochemistry.[4] From the appropriate ratio given above, k_{-1} is *ca.* $10^{4{\cdot}7}$ s^{-1}. The high pressure limiting rate constant is likely to be greater than this and therefore $\Delta G_{-1}^{\ddagger} \leqslant 60$ kJ mol^{-1} (14·3 kcal mol^{-1}). The combined uncertainties are not likely to exceed ±10 kJ mol^{-1}. A value slightly greater than the allyl stabilisation energy[6] (52 kJ mol^{-1}) is to be expected[7] since the radical must lose the unpaired electron delocalisation in rotating to the transition state.

Our value of $\Delta G^{\ddagger}$ is significantly less than that (*ca.* 88 kJ mol^{-1}) obtained recently by Crawford and his co-workers[8] who claim to have observed the competition between isomerisation and recombination for this radical. The interpretation is based on differences in the distribution of radical dimers when different radical precursors are used. These differences are very small and amount only to between 0·1—0·5% of the *total* dimer produced and we doubt the claimed statistical significance.

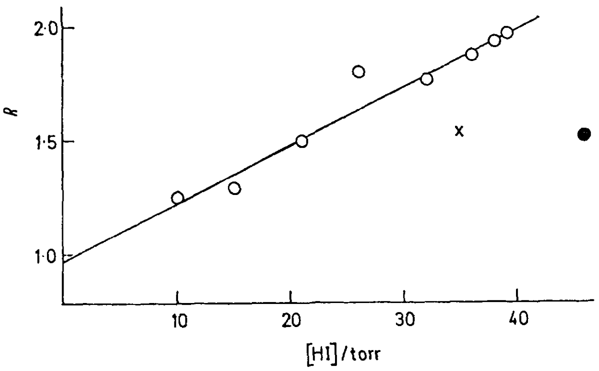

Figure. *The variation of* R (= [cis-*but*-2-*ene*][trans-*but*-2-*ene*]) *with* $[\mathrm{HI}]_0$ *in the products of* HI *and butadiene at* 90°.
○, $[C_4H_6]_0$ = 10 torr; ●, $[C_4H_6]_0$ = 40 torr; ×, $[C_4H_6]_0$ = 10 torr, $[N_2]$ = 34 torr.

The reactions studied here offer an example of a more general technique whereby unimolecular radical reactions can be studied through their competition with the trapping reaction by HI, provided the appropriate iodide (radical precursor) can be made *in situ* at the necessary reaction temperature.

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