The Mechanism of Thermal HI Addition to Conjugated Dienes

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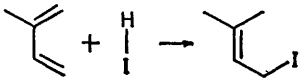
Summary Evidence is presented in support of molecular addition of HI to conjugated dienes *via* a six-membered ring cyclic transition state.

THERE is much evidence[1,2] to support the view that, in the gas phase, both the addition of hydrogen halides to olefins and the reverse elimination of hydrogen halides from alkyl halides proceed *via* a molecular four-centre cyclic transition state. In some experiments with HI and penta-1,3-diene Egger and Benson[3] noted a faster addition rate than expected and attributed it to an abnormally large activating effect of a vinyl substituent on the four-centre addition. The addition of HI to butadiene is similarly fast. In these studies, product iodides were not identified. We now report preliminary results for the gas phase addition of HI to isoprene at 425 K. Our rate data, based on pressure change, indicate second-order kinetics with a rate constant of 5·1 ± 0·7 l mol^{-1} s^{-1}. The major products are 2-methylbut-2-ene, 3-methylbut-1-ene, and I_2 together with small amounts of an iodide whose retention on a column of Durapak, 80—100 mesh OPN coated Porasil C (Waters Associates) coincided with that of a sample of 4-iodo-2-methylbut-2-ene prepared by the liquid phase addition of HI to isoprene at room temperature and identified by n.m.r. As in the earlier studies[3,4] on HI additions to dienes these results suggest a rate-determining molecular addition of HI to diene followed by the known[5] fast reaction of allylic iodide with further HI (*via* an I atom chain) to form olefin and I_2.



(1)

Relative rates of HI *addition to some olefins and dienes at* 425 K

Olefin or diene	Relative rates[a] (i)	(ii)	Ref.
$MeCH{=}CH_2$	1		b
$Me_2C{=}CH_2$	4·1 × 10^2		c
$CH_2{=}CH{-}CH{=}CH_2$[d] ..	3·6 × 10^4	1	e
$MeCH{=}CH{-}CH{=}CH_2$[d] .. (*cis* + *trans*)	3·0 × 10^5	8·3	f
$CH_2{=}C(Me)CH{=}CH_2$ ..	1·1 × 10^6	31	g

[a] Calculated from rate data given in the reference papers and referred to either propylene (i) or butadiene (ii). [b] S. Furuyama, D. M. Golden, and S. W. Benson, *J. Chem. Thermodynamics*, 1969, **1**, 363. [c] A. N. Bose and S. W. Benson, *J. Chem. Phys.*, 1963, **38**, 878. [d] No corrections applied for possible path degeneracy factors. [e] Ref. 4. [f] Ref. 3. [g] This work.

Although the iodide formed is suggestive of the process shown in reaction (1), the possibility of prior formation of another iodide which subsequently isomerises to the observed (thermodynamically favoured) iodide, cannot be ruled out. However, two pieces of information lead us to prefer the six-centre cyclic process rather than the four-centre: (i) Rates of addition of HI to dienes are all very much faster than to structurally analogous olefins. Some relative rates are shown in the Table. If the mechanism were four-centre this would imply a vinyl group substituent effect which enhanced the rates of both additions and reverse iodide decompositions by factors of $10^{4\cdot2\pm0\cdot8}$ ($\Delta\Delta G^{\ddagger} = 34 \pm 7$ kJ mol^{-1}) relative to alkyl substituents. However, in the known four-centre elimination reactions of organic chlorides, vinyl and alkyl group substituent effects are similar[1]. (ii) The rate enhancement for addition of HI to isoprene relative to butadiene (see Table) corresponds to $\Delta\Delta G^{\ddagger} = 12$ kJ mol^{-1} whereas a value of 21 ± 2 kJ mol^{-1} would be expected for a four-centre mechanism. Alkyl substituent effects are known to be less for the six-centre than for the four-centre process in HCl eliminations.[5,6]

The HI addition reaction to dienes complements the behaviour of certain allylic chlorides which eliminate HCl by a six-centre process in preference to a four-centre alternative.[6,7] These findings are further supported by recent calculations based on an electrostatic model.[8]

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