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THE GAS PHASE ADDITION OF HYDROGEN BROMIDE TO ALLENE

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Kovachic and Leitch (1) and Griesbaum, Oswald and Hall (2) have observed that the photoinitiated addition of hydrogen bromide to allene yields exclusively 2-bromo-1-propene, the former working with liquid phase addition at -78°, the latter with gas phase addition at ambient temperature. This orientation contrasts with thiol addition (3), where attack is largely at the terminal carbon by the thiyl radical ($CH_3S\cdot$, $CH_3COS\cdot$ and $C_6H_5S\cdot$), and with addition of CF_3I, where the product is reported to be exclusively that which results from attack on the terminal carbon by the CF_3 radical (4). Inasmuch as thiyl radicals and the trifluoromethyl radical are believed to be electrophilic radicals, similar in character to the bromine atom, the results seem contradictory, and a more critical examination of the HBr-allene reaction was undertaken in these laboratories.

The gas phase, photoinitiated addition of hydrogen bromide to allene was carried out over a range of temperatures from 50° to 150° and with a variety of allene-HBr ratios ranging from 10:1 to 1:10, and at pressures of 10 to 80 mm. Added CCl_4 (72 mm) or $CHCl_2F$ (400 mm) did not change the rate of the addition or the product, which was cleanly 2-bromo-1-propene. No trace of the isomeric methylacetylene could be found even in reactions run 95-98% completion. The kinetics, followed by decrease in pressure, were cleanly first order in HBr under the conditions specified and independent of the concentration of allene. Good Arrhenius plots were obtained under all conditions, giving an activation energy of 4.52 ± .20 kcal/mole.

The reaction of allene with hydrogen bromide contrasts markedly with the reaction of olefins with isolated double bonds with the same reagent (5) in the following respects: (a) the allene-HBr reaction is kinetically first order, while other olefins show kinetics dependent on both olefin and HBr concentrations, (b) the allene-HBr reaction has a positive activation energy, whereas ethylene, for example, has a negative activation energy of -7.5 kcal/mole, and (c) allene is so efficient in scavenging bromine atoms that the most reactive olefin previously investigated, isobutene, does not yield any isobutyl bromide in competition with allene at 100° until all of the latter has been consumed, even at 4:1 ratios of isobutene to allene. At 50°, however, where allene is less reactive and isobutene more reactive, the reaction of a 15:1:1 mixture of HBr:allene:isobutene yields a trace of isobutyl bromide of the order of 0.5% of the yield of 2-bromo-1-propene. (Isobutene is about 200 times more reactive than ethylene toward HBr at 50°(5)).

The difference in kinetic behavior between allene and other olefins with isolated double bonds can be explained most readily in terms of the thermodynamics of the reactions. Using available data and making some approximations by the group contribution method of Andersen, Beyer and Watson (6), the energy-reaction coordinate diagrams of ethylene and allene in reaction with HBr are constructed as shown in Fig. 1. Neither ethylene nor allene may be expected to have an appreciable activation energy in reacting with a bromine atom (7). Ethylene gives an exothermic reaction (E→F, Fig. 1) of about 7.4 kcal/mole (7) (presumably the -7.5 kcal/mole measured from Arrhenius plots in this laboratory). The reaction of allene with bromine atoms (A→B, Fig.1) may be expected to be about 8 kcal/mole more exothermic than the corresponding ethylene-Br atom reaction, since Kistiakowsky, Ruhoff, Smith and Vaughan (8) have shown allene to be that unstable relative to ethylene in hydrogenation experiments. The initial allene-Br atom reaction intermediate may then alter structure or conformation to give resonance stabilized 2-bromoallyl radical (B',

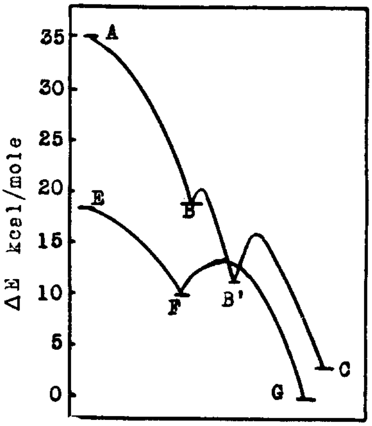

FIG. 1

A. Allene
B. Br-allene radical
B'. 2-Bromoallyl radical
C. 2-Bromo-1-propene
E. Ethylene
F. Bromoethyl radical
G. Ethyl bromide

Fig. 1). The initial radical, B, Fig. 1, might be either the 2-bromoallyl or the $BrCH_2-\dot{C}=CH_2$ radical, but rather more likely the latter. The energy barrier B→B', Fig. 1, is unknown, but probably rather small. Finally, the activation energies for the hydrogen abstraction reactions are 2.3 to 3.0 kcal/mole for the bromoethyl radical (F→G, Fig. 1)(7,9) and 4.5 kcal/mole for the 2-bromoallyl radical (B'→C, Fig. 1) from our kinetic experiments. The small barrier in the HBr-bromoethyl radical reaction is still large enough to produce reversibility in the preceeding step, the formation of the bromoethyl radical (F→G, Fig. 1) because of the favorable competition of unimolecular decomposition of that radical <u>vs.</u> bimolecular hydrogen abstraction. The much larger barrier in the hydrogen abstraction by 2-bromoallyl radical is of small consequence since the much higher exothermicity of the allene-Br atom reaction traps all the 2-bromoallyl radicals formed. Thus, bromine atoms, formed either from the primary photochemical process or from dissociation of bromoethyl radicals, react irreversibly with allene, and the sole product of these competitions is the adduct of the allene-HBr reaction.

On the basis of these thermodynamic data and kinetic evidence one can deduce that the sequence of events in radical additions to allene is probably attack on a terminal carbon, rearrangement when that is possible to an allylic resonance stabilized radical, and, finally, hydrogen abstraction. This series of events can, therefore, explain the observed orientation of attack on allene by various radicals. Additional thermodynamic and kinetic data are highly desirable. In any case, achievement of allylic resonance as a driving force in the initial radical-allene reaction would seem to be of little thermodynamic consequence, and can probably be ruled out.

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