

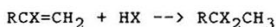
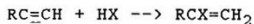
## GEOMETRY AND MARKOVNIKOV'S RULE

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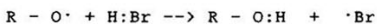
As originally stated in 1869 by Vladimir Markovnikov<sup>1</sup>, when considering the addition of a hydrohalide to an alkene, "the hydrogen atom adds to the carbon of the double bond with the greater number of hydrogen atoms". An example of this addition is the reaction of HCl with propene  $\text{CH}_2=\text{CHCH}_3$ . In this reaction we see that the H (from the HCl) attaches to the carbon atom of the double bond that already has two hydrogen atoms while the Cl attaches to the other carbon atom of the double bond -- which has only one hydrogen atom. Modern day textbooks, such as Solomons<sup>2</sup>, Streitwieser & Heathcock<sup>3</sup>, Morrison & Boyd<sup>4</sup>, etc. advises that this reaction is merely an example of an electrophilic addition. "In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon atom of the double bond so as to yield the more stable carbocation as an intermediate"<sup>5</sup>. This is expressed as a two step mechanism -- with the slow (rate determining) step being the addition of the hydrogen atom to the  $\text{CH}_2$  group and the + charge (thereby forming a carbocation) being localized on the CH group. This is further illustrated by the addition of ICl to 2-Methylpropene. For such a reagent the positive portion is the iodine; consequently, in Step 1, the  $\text{I}^+$  attaches to the double bond with the I going to the  $\text{CH}_2$  part of the molecule and the positive charge localizing on the carbon atom of the  $\text{C}(\text{CH}_3)_2$  part. In the subsequent step the  $\text{Cl}^-$  neutralizes the charge and forms the final product 2-Chloro-1-iodo-2-methylpropane.

Not only is this "rule" useful for addition to a double bond, it may also be applied to addition to a triple bond:<sup>6</sup>



In a similar manner, those reactions known as anti-Markovnikov, such as the addition of HBr in the presence of peroxides, are explained in terms of the homolytic division of the HBr into two free radicals, followed by the addition of the large bromine radical to the double bond, and the subsequent addition of the small hydrogen radical. This anti-Markovnikov addition, often referred to as "the peroxide effect"<sup>7</sup>, is based on the work of Kharasch et al<sup>8</sup>, who claimed that "the orientation of addition of hydrogen bromide to a carbon carbon double bond is determined solely by the presence or absence of peroxides"<sup>7</sup>.

If peroxide is the initiating agent, then there results the formation of a bromine free radical without an accompanying hydrogen free radical:



and thus the free radical mechanism ascribed by all of these authors is the one that is applicable.

Although neither Solomons<sup>2</sup> nor Streitwieser<sup>3</sup> acknowledge the existence of anti-Markovnikov addition in the absence of peroxides (ala Kharasch<sup>8</sup>), Morrison<sup>9</sup> advises that "... anti-Markovnikov addition is caused not only by the presence of peroxides but also by irradiation with light of a wavelength known to dissociate hydrogen bromide into hydrogen and bromine atoms."

Note that the above reaction of irradiated HBr gives no rationale for assuming the order of the free radical reaction (bromine first, followed by hydrogen). In fact, with homolytic division of the HBr, one would expect either the two fragments

would have the same momentum or else the smaller one would have less inertia to overcome and thus would travel faster. In either case, the justification for the addition of the Br $\cdot$  first is highly suspect.

Another explanation for both Markovnikov and anti-Markovnikov reactions can be given purely in terms of the geometry of the molecules. Our premise is that once the homolytic vs. heterolytic division of the HBr has been predetermined by the environment, in all cases, the larger volume of the attacking group will preferentially seek the less hindered environment about the double bond.

First, consider the heterolytic division of HBr into H $^+$  and Br $^-$ . For this reaction, because the breaking of the double bond involves reacting with the pi electrons (i.e., negatively charged) the attacking agent is the positively charged proton. Because of electrostatics, we view the situation as though there is only one particle attacking. Consequently, this particle will preferentially attack from that direction in which it will be least hindered. This is determined by the other substituents on the two carbon atoms. Since hydrogen atoms are much smaller than carbon atoms, the less hindered of the two carbon atoms that comprise the double bond is the one that already has the most hydrogen atoms on it. Only after having formed the carbocation, will the bromine atoms be attracted electrostatically. It will thus add in the only location available.

Next, consider the homolytic division of HBr into H $\cdot$  and Br $\cdot$ . For this reaction, since the free radicals are not charged, without a compelling reason to the contrary, both radicals will attack the pi electrons of the double bond and try to form a bond. In the presence of peroxide there is such a compelling reason to favor one radical over the other (as stated above); however, in the case of a high energy environment, such as from

ultraviolet light, we propose another explanation for these anti-Markovnikov reactions: Because the two free radicals  $H\cdot$  and  $Br\cdot$  are of vastly differing size, we anticipate that the larger  $Br\cdot$  will be accommodated by the "open spaces" about  $CH_2$  leaving the smaller  $H\cdot$  to accept the more confined environment of the  $CH_3CH$  portion of the molecule. In this description there is no need for priority of attack by the larger  $Br\cdot$ , the geometry alone will favor one radical or the other at each site.

In other words, the only purpose for segregating into Markovnikov vs. anti-Markovnikov additions is to emphasize whether the reaction is progressing because of carbocations or free radicals. The driving mechanism is, **AS ALWAYS**, the geometry of the reactants.

#### REFERENCES

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7. Ibid #4, p. 309
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