

MOLECULAR MECHANISM OF HYDROGEN BROMIDE ADDITION TO OLEFINS

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Abstract—Experimental results on the products and the kinetics of the hydrogen bromide addition to alkenes-1 in non-polar solvents and on complex formation in hydrogen bromide-olefin-solvent systems are reviewed. Theoretical calculations concerning hydrogen bromide-olefin complexes are used along with the experimental evidence to suggest a molecular mechanism of addition involving intermediate cyclic structures.

Addition of hydrogen bromide to olefins belongs to classical reactions of organic chemistry. It was used to formulate the well-known Markovnikov's rule which determines the regioselectivity of addition to asymmetric olefins.¹ According to this rule, alkenes-1 should yield the so-called normal addition products, i.e. 2-bromoalkanes. At present it is commonly accepted that the normal addition of hydrogen halides to olefins proceeds via an ionic mechanism. In acetic acid and similar media the most likely trimolecular mechanism Ad_E3 involves a molecule of the olefin and two molecules of hydrogen halide.²

The anti-Markovnikov addition with the formation of abnormal products, namely 1-bromoalkanes from alkenes-1, is usually explained in terms of the so-called peroxide effect investigated in detail by Kharash and Mayo³ and independently by Hey and Waters.⁴ The influence of peroxides on the direction of addition of hydrogen bromide appeared consistent with a radical-chain mechanism.^{5,6} From this standpoint the occurrence of anti-Markovnikov products is typically regarded as testifying to the same mechanism.^{2,7}

The ionic and the radical chain mechanism agree well with the reaction patterns in polar solvents or in the presence of radical initiators such as peroxides or UV radiation. At the same time they can not account for certain facts observed in studies of hydrogen bromide addition to olefins in non-polar media. Indeed, in solvents with a low dielectric constant the presence of ionic species is hardly possible or at least should require a considerable activation energy. Nevertheless it was shown that normal addition of HBr to propylene in pentane at 30° is only 2-3 times as fast as at 0°, which means the activation energy is low (from 16 to 25 kJ/mole).⁸

The ionic and the radical-chain mechanism are also at variance with abnormal addition in the absence of peroxides or other radical initiators. The first reaction of this type to be observed was apparently the addition of HBr to pentene-1 in acetic acid and *n*-hexane solution (reported in 1934⁹). Later these findings were found to be irreproducible and were doubted.¹⁰ Significantly, even the authors of the pioneer study concerning the peroxide effect reported poor reproducibility.³ Other intriguing facts were the abnormal addition in the presence of typical inhibitors of radical-chain processes (2,4-di-*tert*-amylphenol, thiophenol and thiocresol,⁸ 2,6-di-*tert*-butyl-*p*-cresol¹¹) and a change in the direction of HBr

addition to propylene as the reaction mixture was diluted with pentane.⁸

Accordingly, the reaction pattern of hydrogen bromide addition to olefins in non-polar media agrees neither with the ionic nor with the radical-chain mechanism. In certain papers, for instance,¹² it was argued that hydrogen halides may add to olefins by a molecular mechanism without the formation of intermediate ions or radicals. No experimental evidence supporting this suggestion was available until recently. However, some newly obtained data^{13,14} along with the results of quantum-mechanical calculations of molecular interactions in HBr-olefin systems have since made it possible to develop a new viewpoint on the mechanism of HBr addition.

In the present paper the addition of hydrogen bromide to olefins in non-polar media in the absence of radical initiators will be considered in terms of the molecular mechanism.

Products of hydrogen bromide addition

Addition of HBr to heptene-1, octene-1 and cyclohexene was carried out in non-polar solvents (*n*-hexane, freons, carbon tetrachloride) over a broad temperature range. In the absence of peroxides, oxygen and light the reaction proceeds to 100% conversion. With the reagents in an equimolar ratio the products are a mixture of those resulting from normal and from abnormal addition. The composition of this mixture depends on the reagents ratio, their absolute concentrations and temperature: both normal and abnormal products may be obtained in a quantitative yield. The selectivity of addition lends itself to inversion by a change in the reagents ratio (Table 1).

As is seen from the table, an excess of hydrogen bromide promotes Markovnikov's reaction pattern, while excessive olefin leads mainly to abnormal products. In both cases the reaction selectivity is greater at lower temperatures.

Reaction kinetics

In non-polar solvents alkenes-1 add hydrogen bromide in either a normal or an abnormal manner. Hence the reaction kinetics (exemplified by HBr addition to heptene-1 in *n*-hexane) was investigated in two concentration regions, i.e. with the olefin in excess (when 1-bromoheptane is formed) and with excess HBr (when the product is 2-bromopentene).

With excess hydrogen bromide the kinetics of normal

Table 1. Inversion of selectivity of octene-1 hydrobromination in *n*-hexane solution

[HBr] ₀ , M	[C ₈ H ₁₆] ₀ , M	T, K	Yield, %	
			1-bromooctane	2-bromooctane
0.4	3.2	298	95	5
0.4	3.2	195	100	—
1.5	0.1	298	4	96
1.5	0.1	195	2	98

addition in the general form is described by an equation

$$w_n = k_n[\text{OI}][\text{HBr}]^m \quad (1)$$

where m is a variable ranging from 2 at $[\text{HBr}] < 0.2\text{M}$ and $T = 293\text{K}$ to 0 at $[\text{HBr}] > 2\text{M}$ or $T \leq 240\text{K}$. The temperature dependence of the initial reaction rate at constant reagents concentration is not trivial. Indeed, the negative temperature coefficient observed at certain concentrations and temperatures proves to be positive at lower temperatures (Fig. 1).

With excessive olefin the kinetic equation may be written as

$$w_n = k_n[\text{OI}]^n[\text{HBr}] \quad (2)$$

where n , the order in the olefin, depends on the olefin concentration and temperature. At $[\text{OI}] > 0.2\text{M}$ $n = 2$ at 298 K and $n = 0$ at 250 K. The temperature dependence of the reaction rate is similar to that in the case of normal addition. At 298–250 K the negative temperature coefficient is observed, with $E_{\text{eff}} = -13 \pm 2\text{ kJ/mole}$.

Molecular mechanism of hydrobromination

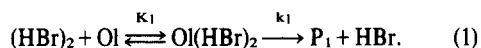
A. Markovnikov's addition. The results on the normal addition of hydrogen bromide to alkenes-1 in *n*-hexane can not be explained in terms of the ionic mechanism, since the observed increase in the yield of 2-bromoalkanes upon dilution of the mixture with a non-polar solvent is inconsistent with participation of ionized species in the reaction. Moreover, in contrast to the

predictions based on the ionic mechanism, the activation energies of HBr addition in media with a low dielectric constant are small or even negative.

The feasibility of an ionic reaction was also investigated by studying the effect of the solvent polarity on the rate of addition. Ionic reactions typically show drastic acceleration with increasing dielectric constant ϵ of the medium. As suggested by Kirkwood's equation, for such reactions the electron transfer extent in the transition state q^* should be close to unity.¹⁵ We have investigated the effect of ϵ on hydrobromination of heptene-1 in *n*-hexane-CH₂Cl₂ mixtures of various compositions. At 298 K an increase in ϵ from 2 to 7 accelerates the reaction only fourfold, and at 250 K does not affect the reaction rate at all. Calculations based on Kirkwood's equation show that the dipole moment of the transition state is low in this case and q^* at 298 K does not exceed 0.4. This ϵ -independent behaviour can not be explained by means of the ionic mechanism.

We believe that normal addition of hydrogen bromide to alkenes in non-polar media proceeds by a molecular mechanism which should encompass the experimental evidence on molecular interactions in the HBr-olefin system. In non-polar solvents hydrogen bromide gives rise to a dimer (the enthalpy of dimerisation in *n*-hexane is -24 kJ/mole^{14}) and the formation of 1:1 and 2:1 complexes with olefins is highly probable (such complexes were observed by IR spectroscopy at low temperatures¹⁶). In view of these data it appears that normal addition involves simultaneous rearrangement of bonds in a complex not preceded by ions or radicals.

At low temperatures ($T \leq 250\text{K}$) and high concentrations of hydrogen bromide ($[\text{HBr}] \geq 2\text{M}$) the latter largely forms a dimer¹⁴ and the reaction may be described by the following kinetic scheme:



Assuming the equilibrium is attained rapidly as compared to the reaction rate, $[\text{HBr}] \gg [\text{OI}]$ and $[(\text{HBr})_2] = 0.5[\text{HBr}]$ we arrive at the following equation for the reaction rate:

$$w_n = k_1[\text{OI}(\text{HBr})_2] = \frac{k_1 K_1 [\text{OI}][\text{HBr}]^2}{2 + K_1[\text{HBr}]} \quad (3)$$

The other limiting case is observed at high temperatures and low concentrations of hydrogen bromide, when its dimerisation may be neglected and the reaction scheme assumes the form of

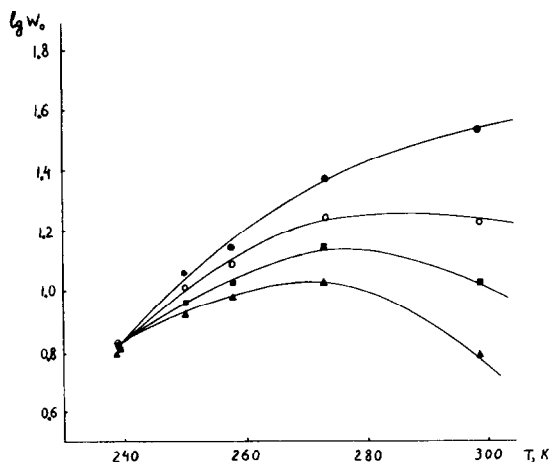
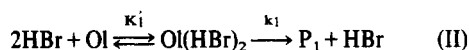


Fig. 1. Initial rate of 1-heptene hydrobromination (in relative units) in *n*-heptane solution vs. temperature and concentration of HBr: $[\text{C}_7\text{H}_{14}]_0 = 0.02\text{M}$, $[\text{HBr}]_0 = 0.12\text{M}$ (1), 0.16M (2), 0.20M (3) and 0.28M (4).

whereas the reaction rate is described by the equation

$$w_n = k_1[\text{O}(\text{HBr})_2] = \frac{k_1 K_1 [\text{O}][\text{HBr}]^2}{1 + K_1 [\text{HBr}]} \quad (4)$$

Equations (3) and (4) suggest that the reaction order in hydrogen bromide may range from 0 to 2 depending on the ratio of the denominator terms, i.e. on the reaction conditions.

This scheme is also in accordance with the temperature dependence of the reaction rate. If we express the rate constant and the equilibrium constant in (3) and (4) as functions of temperature it will be possible to calculate (from the extremum condition $dW_n/dT = 0$) the temperature T_{max} which corresponds to the maximum reaction rate of (I) or (II):

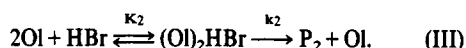
$$T_{\text{max}} = \frac{|\Delta H|}{R\{\ln(|\Delta H|/E_1 - 1) - n \ln[\text{HBr}]\} + \Delta S} \quad (5)$$

where ΔH and ΔS are the enthalpy and the entropy of formation of the $\text{O}(\text{HBr})_2$ complex, E_1 the activation energy of the stage at which the complex transforms into the product, $n = 1$ for scheme (I) and $n = 2$ for scheme (II). Equation (5) points out that an increase in HBr concentration and the relevant increase in the proportion of the complex-bound olefin should increase T_{max} , as is in fact observed (Fig. 1). The negative temperature coefficient and an extremum of the reaction rate vs. temperature curve may be observed provided $E_1 < |\Delta H|$. The greatest possible value of the activation energy is $E_{\text{eff}} = E_1 + \Delta H < 0$ (not considering the temperature dependence of the pre-exponential factor). At low enough temperatures, when virtually all the olefin is bound in a complex, the initial reagent is $\text{O}(\text{HBr})_2$ and $E_{\text{eff}} = E_1 > 0$. Therefore the scheme involving $\text{O}(\text{HBr})_2$ agrees with all the experimentally observed features of the reaction.

B. Anti-Markovnikov addition. The aspects of hydrogen bromide abnormal addition to alkenes-1 observed in the present study can not be described in terms of the commonly accepted radical-chain mechanism. Convincing evidence on the absence of the peroxide effect in the system was obtained as the process was carried out with an inhibitor, i.e. ionol (2,6-di-*tert*-butyl-*p*-cresol). Addition of 0.07M of the inhibitor (10% of the initial HBr concentration) at tenfold excess of the olefin did not change the yield of 1-bromoheptane. In a control run, the same concentration of ionol suppressed the faster UV-initiated radical-chain hydrobromination of heptene-1.

The radical-chain mechanism fails also to account for the fact that the yield of the abnormal product does not depend on the surface to volume ratio of the reaction vessel. A 20-fold increase in this ratio (accomplished by inserting glass capillaries into the reaction mixture) did not change the product composition.

These facts, as well as the reaction kinetics, may be understood with the help of the molecular mechanism. It seems very likely that complex formation is involved in the reaction, the complex consisting of two olefin molecules and a hydrogen bromide molecule:



The kinetic equation corresponding to this scheme (pro-

vided the equilibrium is reached rapidly and $[\text{O}] \gg [\text{HBr}]$ is similar to eqn (4):

$$w_a = k_2[(\text{O})_2\text{HBr}] = \frac{k_2 K_2 [\text{HBr}][\text{O}]^2}{1 + K_2 [\text{O}]^2} \quad (6)$$

This expression explains the observed dependence of the reaction order in the olefin on its concentration. If the enthalpy of complex formation exceeds by its absolute value the activation energy of the complex conversion into the product, the temperature coefficient should be negative. Thus scheme (III) is consistent with the kinetic features of abnormal addition.

Structure of olefin complexes with hydrogen bromide

The low activation energies of the complex-product conversion¹⁴ apparently stem from the cyclic structure of the transition state. In this case the energy required for bond rupture is compensated by that of newly formed bonds and the rearrangement does not require a high activation energy. A molecular mechanism with a cyclic transition state was considered earlier, e.g. for hydrobromination of acetylene derivatives¹⁷ but no definite support for this reaction pattern has so far been reported.

Complexes with low activation energy of rearrangement may to an extent be similar to transition states. To understand the structure of the latter let us consider the structure of hydrogen bromide complexes with olefins. The transition states of normal and abnormal hydrobromination of olefins in non-polar media are likely to contain three molecules of the reagents and should be compared to 2:1 and 1:2 complexes. The relative stability of various complexes and their role in transition state formation can be estimated by sufficiently rigorous quantum-mechanical calculations. The available computation facilities restricted our *ab initio* calculations to 1:1 complexes, which in fact do not directly precede cyclic intermediates. Nevertheless it is reasonable to regard them as the simplest model of molecular interactions in the hydrogen bromide-olefin system.

It is usually thought that 1:1 complexes of olefins with hydrogen halides involve a hydrogen bond, the halide molecule being turned to the double bond by its hydrogen atom.¹⁸ However, MINDO/3 calculations for the hydrogen chloride complex with ethylene indicate¹⁹ the plausibility of an opposite orientation with the halogen atom adjacent to the double bond plane.

To find out the optimum structure of the complexes we performed an *ab initio* computation of the ethylene-hydrogen bromide system using the restricted Hartree-Fock approximation and GAISCF programme.²⁰ The minimal basis STO-3G was employed in all the calculations. Convergence at each point was usually attained by 15-16 iterations, divergence was eliminated by the level shift procedure. The symmetry properties of the nuclear skeleton were disregarded. The distance between the nuclei in the HBr subsystem was taken to be equal to the equilibrium experimental value (1.4146 Å), the ethylene plane served as the XY plane, the geometry of ethylene was optimized by several stepwise iterations. Different orientations of HBr with respect to the ethylene plane at various distances between the plane and the HBr centre of masses were considered.

We have found that as HBr and C_2H_4 molecules approach one another along a normal to the olefin plane, the potential energy surface shows a shallow minimum at

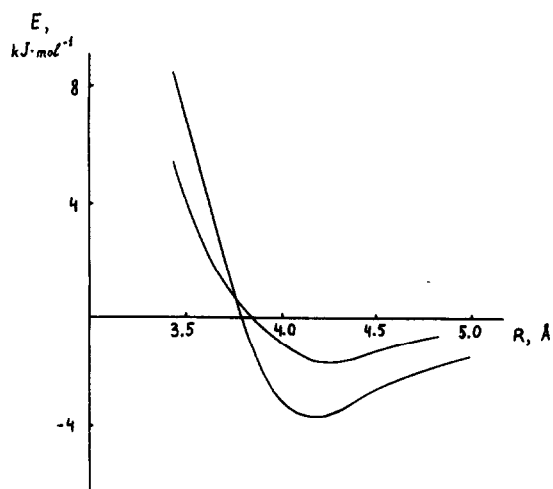


Fig. 2. The energy of the C_2H_4-HBr complex plotted against distance between the bromine atom and the double bond plane R when the HBr molecule is oriented by the bromine atom (1) and by the hydrogen atom (2) to this plane.

both the $HBr \rightarrow OI$ and the $Br-H \rightarrow OI$ orientations (Fig. 2). Orbital analysis for both complexes suggested that only one orbital of HBr ($4p_z$ of the bromine atom) is capable of mixing with ethylene orbitals (π -orbital). In the upper occupied MO of HBr $4p_z$ is the leading orbital. The equilibrium distance between the bromine atom and the ethylene plane is approximately the same in both cases (4.2 \AA when the hydrogen and 4.3 \AA when the bromine is closer to the double bond plane). The calculations have pointed out that the position of the hydrogen atom in the HBr subsystem or, which is the same, the orientation of the HBr molecule, is far less important than the Br position: the hydrogen atom in the $HBr-C_2H_4$ system moves rather freely and exerts no effect on binding.

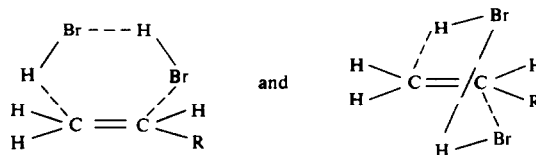
Therefore, the structure of the complex may well involve free or slightly hindered rotation of the HBr molecule about its centre of masses, i.e. actually about the bromine atom. It should also be noted that near the minima the potential curves are fairly smooth, which means the position of bromine itself is not rigid too (Fig. 2).

With other basis sets the quantitative results of our computations could be improved. However, it appears quite reasonable that the qualitative conclusions, particularly that concerning the non-rigidity of the complex structure, provide an adequate general picture of the olefin- HBr interactions and may apparently be extended to 2:1 and 1:2 associates. The experimental data along with the computation results propose a more critical approach to the traditional concept of HX orientation in complexes with olefins: in view of the low energy effects characteristic of the systems under consideration, the generally accepted idea that the HX hydrogen atom is always closer to the olefin plane (as it follows from electrostatic reasoning) seems rather unreliable.

Possible transition state structures in molecular hydrobromination of olefins

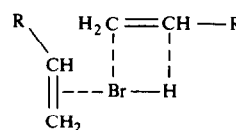
Permanent re-orientation of molecules in complexes may give rise to cyclic structures which permit synchronous breaking of existing bonds and formation of new

ones. For normal addition of hydrogen bromide such structures are



The first structure corresponds to syn- and the second to anti-addition. The labile mutual orientation of the olefin and the hydrogen halide makes the formation of such transition states quite permissible in terms of energy. Their main difference from 2:1 complexes is that the transition state requires a rigid orientation of molecules which prohibits mutual motion at appreciable amplitudes. This should lead to an entropy loss and in this case the free activation energy would be determined almost entirely by the entropy term. Such a mechanism agrees with the experimental finding that the activation energy of rearrangement of the complex into the product is as low as about 20 kJ/mole , while the activation entropy at this stage, as inferred from kinetic evidence, is $200-240 \text{ kJ/mol. deg}$.

In the case of abnormal HBr addition the transition state may be visualized as



The mutual orientation of HBr and one of the olefin molecules is consistent with our computations and with the results reported in.¹⁹ This structure also contains a 4-membered cycle. Such cycles are assumed for gas phase hydrohalogenation of olefins which requires a high activation energy.²¹ In a liquid phase the activation energy may decrease on account of non-specific solvation and specific interactions with the second olefin molecule. From this viewpoint, in abnormal addition the second olefin molecule may be substituted by any strong enough electron donor. Indeed, addition of electron donors in a large amount to a reaction mixture containing no excess olefin sharply increases the yield of 1-bromoalkanes. For example, at $[HBr]_0 = 2.0M$, $[C_2H_4] = 1.4M$ and $T = 298 \text{ K}$ the yield of the abnormal product in hexane was 27%, in toluene 60% and in phenylcyclopropane 99%. These results may be explained as follows. The donor solvent binds an appreciable part of HBr in a $D-Br-H$ complex which reacts with the olefin to form a structure similar to that described above.

The body of evidence obtained in this study suggests, therefore, that addition of hydrogen bromide to olefins in non-polar media basically follows a molecular mechanism. Whether the addition to alkenes-1 would be normal or abnormal depends on the ratio between the reagents and on the reaction temperature.

EXPERIMENTAL

Hydrogen bromide was obtained by adding concentrated hydrobromic acid dropwise to excess P_2O_5 and purified by low temperature vacuum distillation. Portions of HBr were taken using gas pressure measurements with a glass membrane manometer. Prior to every experiment HBr was condensed in a

cold trap at 77 K and slowly heated to a desired vapour pressure. The temperature of solid HBr did not exceed 110 K so that the vapour pressure of possible impurities was negligible. Olefins and solvents were chromatographically pure and peroxide-free. Before the experiments oxygen was thoroughly removed from olefin solutions by repeated freezing, evacuation and melting.

To investigate the composition of reaction products, HBr was condensed in glass ampoules with degassed solutions of the olefin. Upon sealing off, the ampoules were rapidly heated to the melting point of the mixture and after shaking allowed to stay for 24–48 hours in a bath of necessary temperature. Excess HBr, if any, was then removed from the ampoules after they were opened and the reaction products were determined by glc and/or NMR spectroscopy.

The reaction kinetics were followed by fading of the HBr signal in the NMR spectra (if the olefin was in excess) and spectrophotometrically by the decrease in optical density at $\lambda \sim 270$ nm where absorption of HBr-olefin complexes is observed. With excess HBr its distribution between the solution and the gas phase was taken into account.

NMR spectra were recorded by a Varian XL-100 spectrometer. UV spectra were recorded in quartz thermostatted ampoules (i.d. 4 mm) by a Unicam SP-8000 device. Analysis of the bromides was performed using a "Pye Unicam" panchromatograph with a catharometer detector on a glass column (2.5 m \times 0.4 cm) packed with 10% Apiezon L on celite at 398 K.

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