

## Errata: The Absolute Rate of Reactions in Condensed Phases

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tending more and more toward free radical mechanisms. However, Table III suggests that, insofar as the reactions there considered are concerned, in many cases both a molecular and a free radical mechanism may be operative. This is brought out in reactions *a* for Cl, Br, and I, *b* for I, *c* for Cl, Br, and I, *d* for Br and I, and *e* for Cl, where the activation energies for the two mechanisms differ by less than 5 kcal.

### CONCLUSIONS

In the present paper all the arguments concerning the probable course of a reaction, where the reactants may give several different products, are based upon the assumption that the speed of the various reactions determine which products will be formed. This has the advantage of allowing for the possibility of a mixture of products in any proportions (see, for example, reactions *e* and *g*). It was further assumed that the relative rates of several reactions could be predicted from a knowledge of their relative activation energies. This is of course not always safe since the speed of a reaction also depends upon a constant term (the expression for the specific reaction rate constant is taken as  $k = \text{constant} \cdot e^{-A/RT}$ )<sup>28</sup> and upon the concentration of reacting substances. However since *A* enters the rate expression exponentially it is usually the most important term, unless it happens to be nearly equal to zero. Particularly if, for example, two reactions differ in activation energy by 6 or more kcal. their relative rates are predictable with considerable probability unless the concentration of some of the reacting substances is exceedingly small. One exception concerning the reliability of relative activation energies must be noted. This is the

<sup>28</sup> For an evaluation of this constant see Eyring, *J. Chem. Phys.* **3**, 107 (1935). It is also possible that the rate determining step for a reaction involving a proton, may involve a leakage through a potential energy barrier.

case where different mechanisms are involved, and different bonds are being broken, such as reactions *a* and *j*, but not, for example, reactions *a* and *b*. In the case of mechanisms involving free radicals it is seen that we have the interesting case that although two reactions have the same over-all activation energy one is much more probable than the other (reaction *b* and *f* for  $\text{C}_2\text{H}_4\text{Cl}_2$ ).

It has been pointed out many times that relative activation energies can be calculated with more assurance than absolute values.<sup>29</sup> In this paper these relative values constitute the basis of all of our conclusions.

It must also be remembered that, strictly speaking, our conclusions only apply at the beginning of a process, when the reaction is far removed from the stage of equilibrium.

In spite of the above difficulties it seems fairly safe to draw the following conclusions:

1. Chlorine, bromine, and iodine will add to ethylene to form 1,2-dihaloethane rather than the vinyl or ethylidene derivatives.
2. The hydrogen halides of chlorine and bromine will add to the corresponding vinyl compounds rather than react to form ethylene and halogen, whereas the iodine compounds will probably undergo both types of reaction.
3. The symmetrical dihalo derivatives and also the ethylidene compounds of bromine and iodine will decompose to give ethylene and the corresponding halogen, whereas 1,2-dichloroethane and ethylidene chloride will give vinyl chloride and HCl upon decomposition.
4. In most of the reactions considered mechanisms involving free radicals are slightly more probable than the corresponding unimolecular or bimolecular reactions.

We wish to express our appreciation to Professor Farrington Daniels for his constant interest and help in this problem. One of us (A. S.) wishes gratefully to acknowledge financial assistance from the Wisconsin Alumni Research Foundation.

<sup>29</sup> See, for example, reference 3.

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(*J. Chem. Phys.* **3**, 492 (1935))

ON p. 497, line 12, first column and again in line 14 should read  $(\alpha^*)^{-1}$ . The values of  $\alpha$  for nitromethane and carbon tetrachloride are 0.00233 and 0.00213, respectively. We wish to thank Mr. Frank Brescia for calling this to our attention.