

## The Quantum Mechanics of Chemical Reactions Involving Conjugate Double Bonds

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# The Quantum Mechanics of Chemical Reactions Involving Conjugate Double Bonds<sup>1</sup>

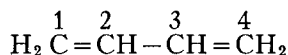
HENRY EYRING, ALBERT SHERMAN AND GEORGE E. KIMBALL, *Frick Chemical Laboratory, Princeton University*

(Received June 2, 1933)

The various theories of conjugate double bonds are discussed on the basis of quantum mechanics. The potential energy surfaces for the addition of diatomic molecules to such bonds are calculated by the generalized Heitler-London method. It is shown that various mechan-

isms are possible for such reactions and that such effects as the steric repulsions of the various inactive groups in the molecule and the nature of the catalytic surface on which such reactions often take place determine whether 1-2 or 1-4 addition takes place.

THE term "conjugate double bonds" is applied by organic chemists to those compounds which contain two double bonds joining pairs of atoms which are joined to each other by a single valence bond. For example in butadiene

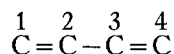


the double bonds joining carbon atoms 1-2 and 3-4 are "conjugate," and in acrolein

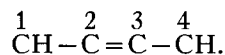


the C=C double bond and the C=O double bond are conjugate.<sup>2</sup>

Under certain conditions such systems of double bonds exhibit abnormal behavior. For example, when molecules containing the group



are hydrogenated it is frequently found that the hydrogen is added, not to atoms 1 and 2 or 3 and 4, but to atoms 1 and 4, a new double bond being formed between atoms 2 and 3:

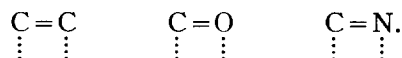


To account for this and similar phenomena,

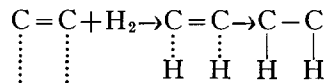
<sup>1</sup> Preliminary reports of this work have been published in *Science News Letter* 23, 5 (1933), and *Science* 77, 158 (1933).

<sup>2</sup> For a fuller discussion of conjugate double bonds see Cohen, *Organic Chemistry*, 5th ed. (Longmans, Green, N. Y.) Vol. 1, pp. 144-163.

Thiele<sup>3</sup> introduced a theory of "partial valencies." According to Thiele atoms joined by double bonds exhibit a residual or partial valence which he indicated by dotted lines

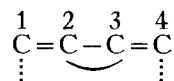


The addition of molecules such as H<sub>2</sub> to such double bonded atoms may then be represented by the following steps:



the hydrogen first being attached by the partial valences, which then rearrange to normal bonds.

In a system of conjugate double bonds the partial valences of the adjoining atoms 2 and 3 would satisfy each other, so that such a system might be represented by



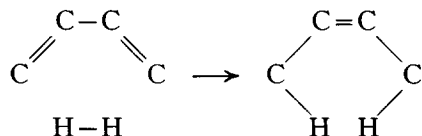
the curved line representing the union of two partial valences. Since atoms 2 and 3 now have no residual valence, addition of molecules such as H<sub>2</sub> might now be expected to take place on atoms 1 and 4, the partial valence bond between atoms 2 and 3 becoming an ordinary double bond.

Another view of this type of reaction has been proposed by Erlenmeyer<sup>4</sup> who regarded the re-

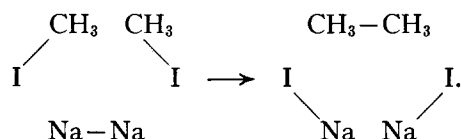
<sup>3</sup> Thiele, *Ann. d. Chemie* 306, 87 (1899).

<sup>4</sup> Erlenmeyer, *Ann. d. Chemie* 316, 43 (1901).

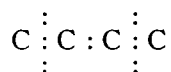
action as a simple rearrangement of bonds



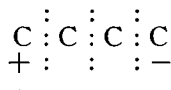
analogous to such reactions as



Other theories have been suggested by Lapworth<sup>5</sup> and by Kermack and Robinson<sup>6</sup> which are based on the Lewis-Langmuir theory of valence. If we represent the conjugate system by the electronic formula



these authors assume that an electron shift occurs to the form



in which one end carbon atom has gained an electron and the other lost an electron, the remaining electrons forming a series of three-electron bonds. The polarity of the end carbon atoms then attracts the molecule which is about to be added.

A quantum mechanical interpretation of the Lapworth-Kermack-Robinson mechanism is difficult. While it is quite possible that the three-electron bonds postulated by them do exist,<sup>7</sup> in the particular case of conjugate double bonds such states almost certainly have a high energy, and cannot therefore be present in any large amount at ordinary temperatures. Moreover, in the case of symmetrical molecules such as butadiene, the polarity would oscillate from one end to the other with a very high frequency, so that the mean charge on any atom would be zero

<sup>5</sup> Lapworth, *Trans. Chem. Soc.* **121**, 416 (1922).

<sup>6</sup> Kermack and Robinson, *Trans. Chem. Soc.* **1212**, 427 (1922).

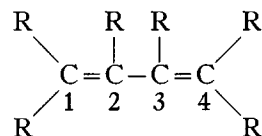
<sup>7</sup> See, for example, Pauling, *J. Am. Chem. Soc.* **53**, 3225 (1931).

during the comparatively slow approach of an additive molecule. This theory cannot therefore be considered satisfactory.

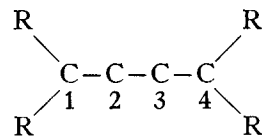
The Thiele theory is not without a quantum mechanical basis. If we consider only the four electrons entering into the two double bonds, it is possible to set up an eigenfunction corresponding to bonds between atoms 1-2 and 3-4 and another eigenfunction corresponding to bonds 1-4 and 2-3. The actual normal state of the molecule has for its eigenfunction a linear combination of these two ways of drawing the valence bonds. Since, however, the interaction energy of two carbon atoms as far apart as atoms 1 and 4 is quite small, the energy of the second system of bonds must necessarily lie much higher than that of the first system and consequently it is to be expected that the normal state of the molecule contains very little of the second way of drawing the bonds. But Thiele's picture of the conjugated system is essentially the second way of drawing the bonds, for the bond between atoms 1 and 4 is so weak that the electrons are practically free. Since we have seen that this way of drawing the bonds is unimportant in the normal state, we must discard Thiele's picture.

Erlenmeyer's hypothesis, on the other hand, seems to be free from any qualitative objections, but an estimate of the activation energy of some typical examples of 1-4 addition reactions is necessary before its validity can be established.

Suppose therefore that we consider the addition of a molecule AB, composed of two univalent atoms, to the conjugate double bonds of some substituted butadiene:

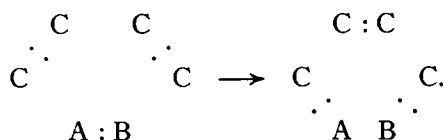


We may regard this molecule as a fixed system



plus four electrons, one on each carbon atom, which normally form the second bond between atoms 1-2 and 3-4. In the Lewis-Langmuir

notation we may then write the essential part of the reaction as



The quantum mechanical calculation of the energy of activation of a reaction in which six electrons take part has been described by Sherman and Eyring.<sup>8</sup> We have carried out this calculation for the case in which A and B are bromine atoms or hydrogen atoms. The constants used to determine the necessary Morse potential energy curves are given in Table I.  $D$  is the heat

TABLE I.

Molecule	$D$	$D'$	$\omega_0$	$r_0$	$a$
C—C	74.5	75.6	1620	1.46	2.11
C—Br	65.3	66.1	557	2.05	1.45
C—H	92	96.2	2920	1.13	1.88
H—H	102.4	108.6	4375	0.74	1.942
Br—Br	45.2	45.7	323.9	2.28	1.98

of dissociation in kg cal.,  $D'$  the heat of dissociation plus the half quantum of vibrational energy,  $\omega_0$  the vibrational frequency in  $\text{cm}^{-1}$ ,  $r_0$  the normal separation of the atoms in A and  $a$  is Morse's constant. In every case it was assumed that the coulombic integral was 14 percent of the total energy.

Assuming that the valences of any carbon atom are directed toward the vertices of a regular tetrahedron, and that when two carbon atoms are joined by a double bond these tetrahedra are placed so that they have an edge in common, the four carbon atoms in the butadiene structure lie in a broken line, the angles at atoms 2 and 3 being  $\arccos(-1/\sqrt{3}) = 125^\circ 16'$ . In the normal state of the molecule there will be free rotation about the single bond joining atoms 2 and 3. The most favorable orientation for 1-4 addition is that in which the four carbon atoms lie in a plane, with atoms 1 and 4 on the same side of the line joining atoms 2 and 3. The atoms A and B of the molecule AB

<sup>8</sup> Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932). See also Taylor, Eyring and Sherman, J. Chem. Phys. **1**, 70 (1933).

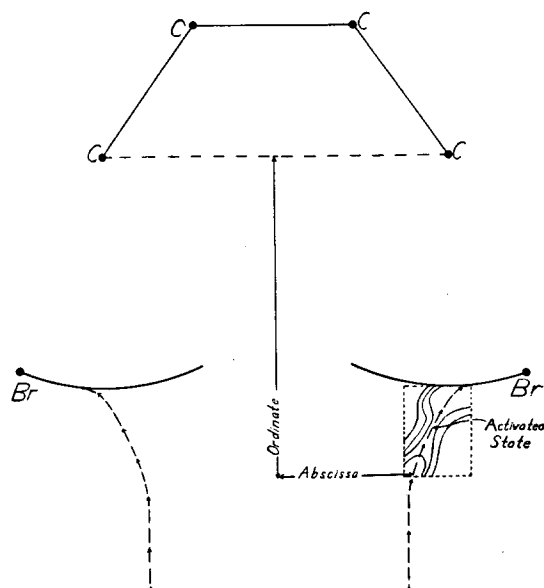
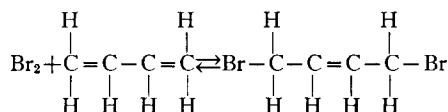


FIG. 1. Addition bromine to the 1-4 carbon atoms in butadiene.



can then most easily approach in the same plane. The situation is shown in Fig. 1 for the case of  $\text{Br}_2$  addition.

If the molecule AB remains symmetrically placed with respect to the carbon atoms the configuration can be completely specified by two coordinates:  $x$ , the distance of the center of the molecule AB from the line joining the two atoms on which addition is to take place, and  $y$ , the distance between the atoms A and B. During the course of the reaction the molecule AB will at first approach the butadiene molecule, that is,  $x$  will decrease, while  $y$  will remain almost constant. Finally, however,  $y$  will begin to increase and the molecule will divide into two atoms attached to carbon atoms 1 and 4.

We have calculated the energy of this system in the two cases when AB is  $\text{Br}_2$  and  $\text{H}_2$  for a sufficient number of values of  $x$  and  $y$  to be able to construct a contour map of the energy as a function of  $x$  and  $y$ . The energy surface shows a valley coming in from  $x = +\infty$ , whose bottom, for large  $x$ , follows the line  $y = r_0$ , the normal distance of the molecule AB. Near the carbon

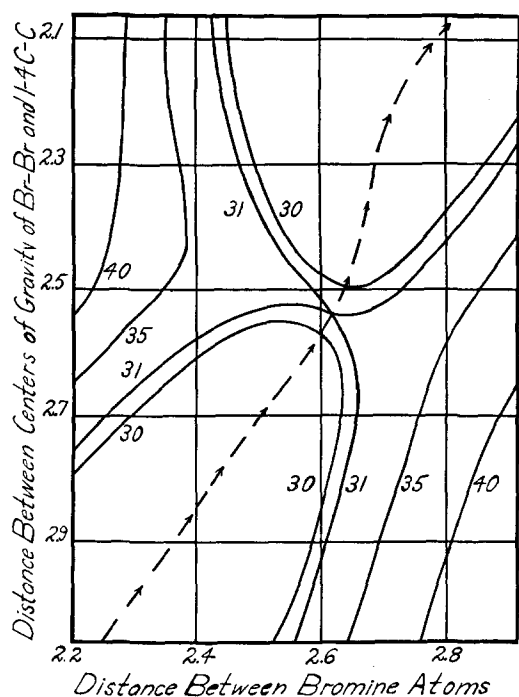


FIG. 2. Potential energy surface for the reaction

atoms the valley turns outward and finally runs into a sort of circular trough at the normal distance for the C-A molecule. The path of the valley floor is shown as a dotted line in Fig. 1. As the path turns the valley floor rises, reaches a maximum height and drops again. An enlargement of the portion of the energy surface near the top of the pass is shown in Fig. 2. It can be seen from this figure that an energy of 31.3 kg calories is required to surmount the potential barrier. A similar surface for the 1-4 addition of  $H_2$  shows an activation energy of 64.0 kg calories.

If the additive molecule does not approach in the same plane as the four carbon atoms, the activation energy is found to be higher. For example, if bromine approaches along a line perpendicular to this plane the activation energy rises to 65.0 kg calories, and if the approach is along a line making an angle of  $109^\circ$  to the plane, the activation energy is 40.3 kg calories. The positions of the activated points and the activation energies for molecules approaching along different paths are shown in Table II. This table gives the activation energies of the molecules AB shown in the first column adding to the carbon

atoms shown in the second column when the line of approach makes the angle given in the third column with the plane of the carbon atoms. The next two columns give the  $x$  and  $y$  coordinates of the system at the activated point.  $Q_{act.}$  is the coulombic binding at this point,  $I_{act.}$  the interchange binding at this point and  $E_{act.}$  the total binding.  $E_0$  is the total binding when the molecule AB is at a great distance from the butadiene molecule, so that  $E_0 - E_{act.}$  is the activation energy of the reaction. The table also includes the results obtained from the calculation of similar surfaces showing the process of 1-2 addition. Examples of these surfaces are shown in Figs. 3 and 4.

From Table II it may be seen at once that it is much easier for addition to take place in the 1-4 position than in the 1-2 position, and that the easiest direction of approach is in the plane of the carbon atoms. These activation energies, however, take no account of the groups which may be substituted on the butadiene molecule. As has been discussed elsewhere<sup>9</sup> the remaining atoms

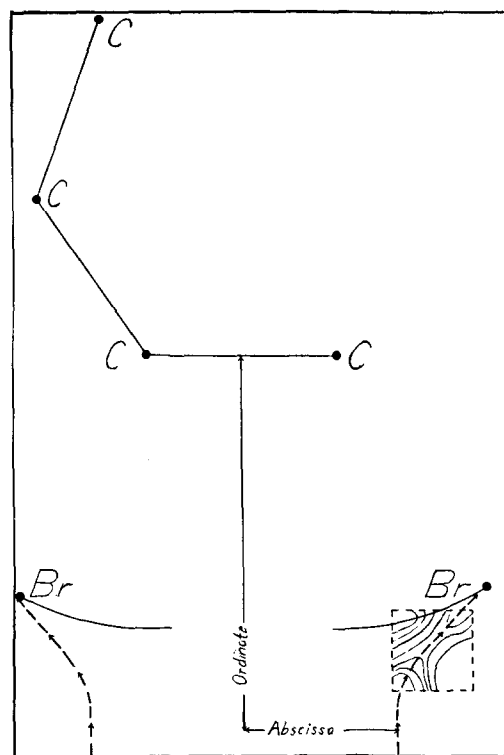


FIG. 3. Addition of bromine to the 1-2 carbon atoms in butadiene.

<sup>9</sup> Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

TABLE II.

AB	Pos.	Angle	$x$	$y$	$Q_{\text{act.}}$	$I_{\text{act.}}$	$E_{\text{act.}}$	$E_0$	$E_0 - E_{\text{act.}}$
Br <sub>2</sub>	1-4	180°	2.5	2.6	64.0	78.2	142.2	173.4	31.3
Br <sub>2</sub>	1-4	109°	2.4	2.6	65.5	67.0	132.5	172.8	40.3
Br <sub>2</sub>	1-4	90°	2.3	2.6	74.2	34.2	108.4	173.4	65.0
H <sub>2</sub>	1-4	180°	2.2	1.1	87.5	84.8	172.3	236.3	64.0
Br <sub>2</sub>	1-2	90°	2.2	2.6	76.7	39.7	116.4	172.6	56.2
Br <sub>2</sub>	1-2	180°	2.1	2.8	69.4	62.3	131.7	173.4	41.7
H <sub>2</sub>	1-2	180°	1.3	0.88	81.9	72.8	154.7	236.3	81.6

of the molecule exert a force equal to one-half the interchange force which would be exerted if there were bonds joining the atoms to the molecule AB, less the coulombic attraction. Thus the substitution of a methyl group for one of the hydrogen atoms on carbon atom 4 might easily create enough repulsion to make 1-2 addition easier than 1-4 addition. The exact calculation of these repulsive forces is however complicated by

the fact that the carbon eigenfunctions are not the spherically symmetric sort postulated in the work just mentioned but instead are concentrated in the tetrahedral directions characteristic of carbon. A simple calculation would therefore greatly overestimate the strength of the repulsions.

Regardless of these repulsions, the activation energies given in Table II are a lower limit, and since these activation energies are all of the order of 30-60 kg calories, these reactions will be extremely slow at room temperatures. Since it is found experimentally that reactions between bromine and conjugated systems are fast reactions in general, we must search for still other possible mechanisms, such as catalysis by a surface.

Heisig<sup>10</sup> has shown that the reaction between gaseous butadiene and bromine takes place largely on the surface of the glass vessel in which the reaction takes place. A detailed consideration of the possible reaction mechanisms on surfaces of various kinds is too complicated to be carried out at present, but certain possibilities may be noted. A very probable mechanism is one similar to that suggested by Sherman and Eyring<sup>11</sup> for the ortho-para hydrogen conversion on catalysts such as activated charcoal.<sup>12</sup> If this mechanism

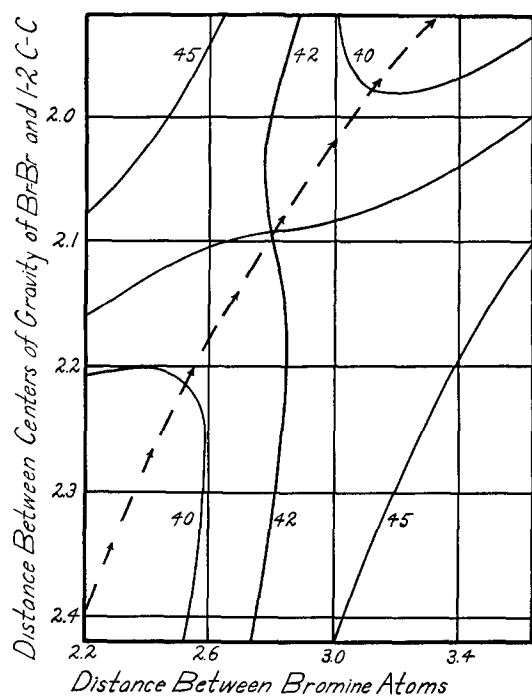
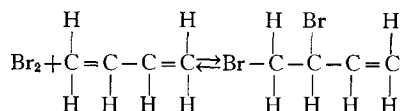


FIG. 4. Potential energy surface for the reaction



<sup>10</sup> Heisig, J. Am. Chem. Soc. **55**, 1297 (1933).

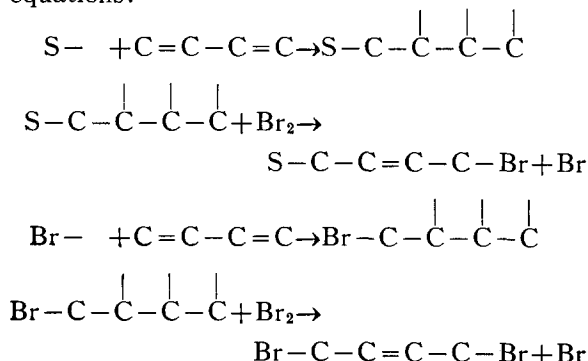
<sup>11</sup> Sherman and Eyring, J. Am. Chem. Soc. **54**, 2661 (1932).

<sup>12</sup> Bonhoeffer, Farkas and Rummel, Zeits. f. physik. Chemie **21B**, 225 (1933), object to this mechanism as an explanation for the ortho-para hydrogen conversion at low temperatures but accept it at room temperature and above. It is for these higher temperatures it is of interest here.

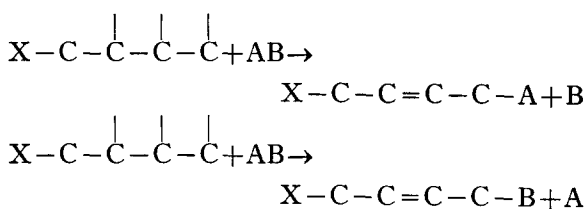
can be extended to the case we are now considering we might regard the conjugate linkage joined to the surface of the catalyst by bonds from carbon atoms 1 and 2 or 1 and 4. The additive molecule might be adsorbed on a nearby portion of the surface. When desorption takes place, both molecules may desorb together and simultaneously form a single molecule. Whether this molecule is the 1-2 or 1-4 addition product depends on such factors as the spacing of the active atoms in the surface and the method of attachment of the butadiene molecule. Further consideration of this mechanism would therefore require more data than are available at present.

Another possible mechanism would involve the attachment of the butadiene molecule to the surface by only one bond, probably to carbon atom 1. This gives a free electron on atom 2 which in turn tends to loosen the electrons on atoms 3 and 4. The electrons on atoms 2, 3 and 4 are then in the same state as the electrons on three univalent atoms. Two of the three electrons will always form a bond between atoms 2 and 3 or 3 and 4, while the third electron will be free. The bond, however, will oscillate rapidly between 2-3 and 3-4, so that the electrons on atoms 2 and 4 are each free half the time. If now a bromine or other additive molecule strikes the free end of the conjugate system, the carbon atom struck behaves very much like a free monovalent atom, and with a small activation energy may attach itself to one of the bromine atoms, leaving the other bromine atom free. A quantum mechanical calculation of the activation energy of this reaction gives 13 kg calories, indicating that the reaction may go at a very rapid rate at room temperatures. The bromine atom resulting can, with a calculated activation energy also of 13 kg calories, curiously enough, add itself to the 1 carbon atom of another butadiene molecule, forming a molecule in a condition similar to that of a molecule attached to a surface, and having the same two half-free electrons. This molecule can then react with a bromine molecule to form a molecule of the dibrom addition product and a new bromine atom

which may carry on the chain. The reaction mechanism may be represented by the following equations:



where S is a surface atom. It might be argued against this mechanism that in the case of the addition of an unsymmetrical molecule AB to the conjugate linkage a mixture of the A-A and B-B addition products should be formed with the A-B addition product. This is not observed. This would, however, not necessarily be true, for in general the activation energies for the reactions



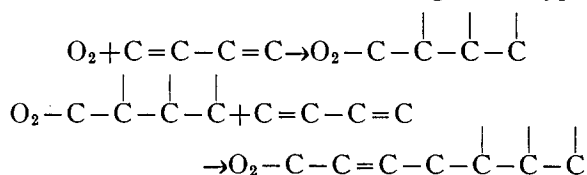
will be sufficiently different that one of them will occur much more readily than the other. Suppose that the first of these reactions predominates. Then the chain will be carried on by the B atoms

alone so that the X in  $\text{X}-\text{C}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}$  will always be B, and only the AB addition product will be formed.

A more serious difficulty with this reaction scheme arises from the fact that the bond  $\text{S}-(\text{C}-\text{C}=\text{C}-\text{C}-\text{Br})$  is much stronger than

the bond  $\text{S}-(\text{C}-\overset{|}{\underset{|}{\text{C}}}-\overset{|}{\underset{|}{\text{C}}}-\text{C})$ , so that the rate of desorption of  $-\text{C}-\text{C}=\text{C}-\text{C}-\text{Br}$  radicals will be slow. The surface will therefore soon become

poisoned and the reaction will stop. For this reason we believe the first surface mechanism to be the more likely in the majority of cases. The second mechanism, however, is probably the course of photochemical addition reactions, the atoms formed by the photochemical dissociation of the additive molecule initiating chains of this type. The rôle played so often by oxygen in polymerizations may well be due to a similar effect, the reaction mechanism being of the type

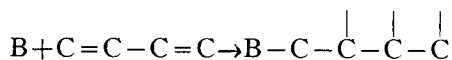


and so on, each successive addition activating the end of the last molecule added to the chain.

Similar reaction chains may sometimes arise from the thermal decomposition of the molecule AB into atoms assuming again that the B atoms carry on the chain. The reaction initiated in this way will have a rate governed by an expression of the type

$$d[\text{BuAB}]/dt = kK^{\frac{1}{2}}[\text{AB}]^{\frac{1}{2}}[\text{Bu}],$$

where  $[\text{Bu}]$  is the concentration of the butadiene molecule,  $[\text{BuAB}]$  is the concentration of the addition product, and  $[\text{AB}]$  is the concentration of AB.  $k$  is the rate constant for the reaction



and  $K$  is the equilibrium constant  $[\text{A}][\text{B}]/[\text{AB}]$ . Now  $K$  varies with temperature essentially according to the law  $e^{-X/RT}$  where  $X$  is the heat of dissociation of AB.  $k$  varies as  $e^{-E/RT}$  where  $E$  is the activation energy of this reaction. Substituting these quantities in the expression for the total rate we find a factor  $e^{-(E+X/2)/RT}$  for the temperature dependence of the rate. In other words the effective activation energy for the whole mechanism is  $E+X/2$ . If this is lower than the activation energy for the direct addition reaction this mechanism will be preferred. We have seen that for  $\text{Br}_2$ ,  $E$  is 13 kg calories and  $X$  is 46 kg calories, so that  $X/2+E$  is 36 kg calories, which is slightly higher than the activation energy of the direct addition process. The difference here is so small that under suitable conditions both reactions may be operative.

From these considerations it becomes clear that the theory of reactions involving conjugate linkages cannot be explained in terms of the structure of the conjugate system alone, for during the course of the reaction this structure may be greatly modified by the other reactant. Further study of the kinetics of these addition reactions may reveal examples of all of the mechanisms we have discussed. There seems to be no general rule for predicting the course of such reactions but the construction of the proper set of energy surfaces in each individual case.