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along the internuclear axis, and the resultant distortion they produce. It is to be expected that for this reason the approximation will be better for greater internuclear distances. How useful it will be in a particular case depends on the accuracy required in the molecular property being calculated. Because of the availability of Kopineck's tables of hybrids for equal effective nuclear charges, and the overlap tables of Mulliken *et al.*, this approximation is extremely simple to use. It may be useful, at least for rough calculations, until the time when tables of hybrids for unequal effective nuclear charges become available.

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The Thermal Dimerization of Butadiene, and the Equilibrium between Butadiene and Vinylcyclohexene

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The kinetics of the dimerization of butadiene and of the dissociation of vinylcyclohexene have been considered in the light of thermodynamic equilibrium calculations. The lack of accord between the results is resolved if the dissociation of vinylcyclohexene is given by the rate expression

$$k_d=5.02\times10^{15}\exp(-61{,}800/RT)\ \text{sec}^{-1}.$$

THREE major kinetic investigations, two on the thermal dimerization of butadiene and one on the depolymerization of dimeric butadiene, have recently been described in the literature. From 446 to 660°K, Kistiakowsky and Ransom[1] found the dimerization to be second order, proceeding by the rate equation

$$k_a=9.20\times10^9\exp(-23{,}690/RT)\ \text{cc mole}^{-1}\ \text{sec}^{-1}.$$

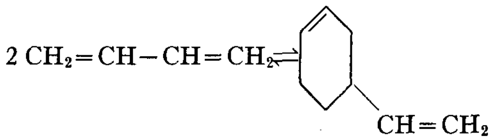
It appeared also that with increasing temperature the activation energy for the dimerization increased. The work of Rowley and Steiner[2] in the temperature range 690–925°K substantiated this. At these temperatures the rate expression obtained was

$$k_a=1.38\times10^{11}\exp(-26{,}800/RT)\ \text{cc mole}^{-1}\ \text{sec}^{-1}.$$

Depolymerization of dimeric butadiene was reported by Doumani[3] and associates to proceed by a first-order mechanism according to the relation

$$k_a=2.35\times10^8\exp(-36{,}000/RT)\ \text{sec}^{-1}$$

in the temperature range 783–977°K. From these data the heat of reaction and equilibrium constants for the reaction



can be calculated. From 750 to 950°K the equilibrium constant is given by the ratio of the forward and reverse rates, and in terms of partial pressure is

$$K_p=5.87\times10^2/RT\exp(9200/RT).$$

The equilibrium constants and free energy changes for this equilibrium from this expression are as shown in Table I.

TABLE I.

T(°K)	750°	775°	800°	825°	850°	875°	900°	925°	950°
K_p	188.6	149.6	120.2	97.9	80.5	67.0	56.2	47.6	40.6
$\Delta F°$(kcal)	−7.81	−7.71	−7.62	−7.52	−7.42	−7.31	−7.21	−7.10	−7.00

TABLE II.

T(°K)	298.1	300	400	500	600	700	800	900	1000
$\Delta F°$(kcal)	−25.7	−25.6	−21.9	−17.9	−14.7	−11.5	−7.9	−4.7	−1.3

The temperature dependence of the free energy change is exceedingly small according to these results. The heat of reaction, is predicted as 9.2 kcal/mole in this temperature range.

Comparison of these data with results from the thermodynamic method shows that only at 800°K is there approximate agreement. The free energy changes for the butadiene-vinylcyclohexene equilibrium were calculated using the van't Hoff Isochore in the modified form

$$\Delta F_T{}^0=I_H+(\Delta a-I_s)T=\Delta aT\ln T-\tfrac{1}{2}\Delta bT^2-\tfrac{1}{6}\Delta cT^3,$$

where the constants I_H and I_S are evaluated from the

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data at 298.1°K. For this purpose the following data were used for vinylcyclohexene: $\Delta H^0f_{298.1}=16.8$ kcal, $S^{\circ}{}_{298.1}=96.4$ cal/deg/mole, $C_p{}^0=-2.22+148.2\times10^{-3}T-62.38\times10^{-6}T^2$. These data were calculated from reference compounds, ethylbenzene,[4] cyclohexane,[4] cyclohexene,[5,6] for which the data are well established, and the method of group increments or contributions.[7,8] The thermodynamic properties of butadiene have been reported elsewhere.[9] The free energy changes thus calculated for the dimerization of butadiene for temperatures up to 1000°K are given in Table II.

In Fig. 1 a comparison is shown of the results from the thermodynamic method and the experimentally established rate equations. The lack of agreement between the two methods is much greater than the errors inherent in the above calculation. The heat of reaction at 25°C calculated from heats of formation is -36.7 ± 0.5 kcal.

The cause of disagreement observed for the two methods is found to lie in the equation[3] for the thermal dissociation of vinylcyclohexene. The frequency factor can be calculated using the statistical expression of the theory[10] of reaction rates:

$$a=Ke^2kT/h(\exp\Delta S_c{}^*/R).$$

The entropy value for this activated complex has been calculated by Wassermann[11] as $S^{\circ}{}_{c600}=120.44$ eu per mole, and the entropy of vinylcyclohexene[1] at 600°K is 112.6 eu. Thus for the dissociation $\Delta S_c{}^*$ is 7.8 eu, and the frequency factor is $10^{15.7}$ if the transmission coefficient is taken as approximately unity (true in many first-order reactions). The energy of activation can be obtained from a knowledge of the heat of reaction at 800°K and the energy of activation for the forward reaction.[2] Using the data for butadiene,[9] and the heat of formation of vinylcyclohexene corrected to 800°K, the heat of reaction $\Delta E^{\circ}{}_{800}=35.0$ kcal. The value for the latter from experimental kinetic data was 9.2 kcal. It is unlikely that the calculated value is in error by more than 2 or 3 kcal. The energy of activation for the dissociation reaction is thus 61.8 kcal/mole. This value is in accord with the order of magnitude for the energy of activation reported[12] for the dissociation of cyclohexene (57.5 kcal) and that previously estimated[1] for dissociation of vinycyclohexene (64 kcal). Accordingly, the rate of dissociation of 3-vinylcylohexene is given by

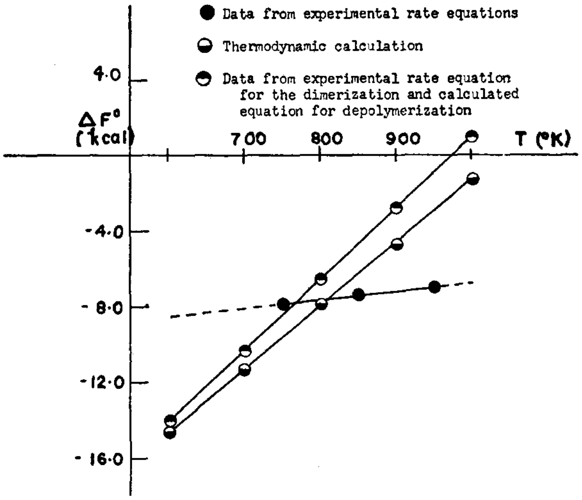

FIG. 1. The free energy change-temperature relation for the equilibrium: $2(CH_2=CH-CH=CH_2)\rightleftharpoons C_8H_{12}$.

$$k_a=5.02\times10^{15}\exp(-61{,}800/RT)\ \text{sec}^{-1}.$$

The expression for the equilibrium constant for the butadiene-vinylcyclohexene reaction is

$$K_p=2.76\times10^{-5}/RT\exp(35{,}000/RT),$$

if the rate equation above is used with the data of Rowley and Steiner. The free energy changes and $\log K_p$ calculated from this equation are in good agreement with the results of the thermodynamic calculation as is shown in Fig. 1.

The frequency factor and activation energy reported by Doumani, Deering, and McKinnis[3] seem to be unusually low for the homogeneous thermal dissociation of vinylcyclohexene and do not lend themselves to equilibrium calculations as seen by the criterion of the thermodynamic methods. The low values may possibly be accounted for by a catalysis or wall effect present but not reported in the investigation.

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