the ratios of k_2/k_1 are unaffected by the presence of additional photochemical initiation. Hence, it would appear that short chains involving fluorine atoms can be initiated on the quartz surface; it is apparent that hydrogen fluoride plays some part in this process, and that the thermal history of the quartz surface is also relevant. Our interpretation of these experiments is further supported by the fact that the calculated ratio k_2/k_1 is independent of fluorine, hydrogen, methane or inert gas pressure, and percentage consumption of the reactants. Furthermore, we can exclude the reaction 4, at least below 60° on the grounds that no reaction took place in the metal vessel in the absence of ultraviolet irradiation, and, judging from the general behavior in the quartz system, we can probably exclude it over the whole temperature range studied, *i.e.*, up to 150°.

DIMERIZATION OF GASEOUS BUTADIENE—EQUILIBRIUM STUDY[1]

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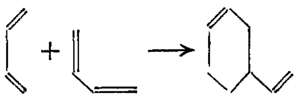
The reaction equilibrium for the dimerization of butadiene and the depolymerization of vinylcyclohexene has been studied in the temperature range from 630–700°K. The results are evaluated in the light of equilibrium calculations from thermodynamic data and reaction velocity constants for this system. The close agreement between the entropy change for this reaction at 600°K. and the entropy of activation for the dimerization suggests a highly circumscribed transition state rather similar in structure to the cyclic product in this process.

Comparatively few experimental studies on reaction equilibria in the homogeneous gas phase have been made. The rate of the gas phase cyclization of butadiene to vinylcyclohexene



(1)

in the temperature range of 200–400° is well established.[3,4] The reaction may be interpreted as a Diels–Alder type process occurring in the gas phase, *i.e.*, uninfluenced by solvent effects. A comparison of the thermodynamically predicted reaction equilibria with values calculated from the rate equations for dimerization[3,4] and depolymerization[5] has also been reported.[6,7] The marked disagreement between the values of the reaction equilibria predicted from thermodynamic data and the rate constants suggested a need for further work. While from the estimated free energy change for the reaction equilibrium at 400°, −9.6 kcal./mole, rather complete conversions of the diene to vinylcyclohexene would be predicted at reaction equilibrium, modern analytical methods such as gas chromatography made an experimental study of the process still seem feasible. The present communication reports the results of some experimental equilibrium measurements in the gas phase at temperatures up to 400° and further theoretical considerations on this fundamental gas phase dienes reaction.

Experimental

Butadiene (1,3-) was a C.P. grade subjected to two simple low temperature distillations before use. It was stored at −78° in 500-cc. glass ampoules fitted with 14/35 standard taper joints and pressure stopcocks. Before use, the butadiene was degassed several times by the conventional manner to remove last traces of dissolved air.

The experimental assembly for the high temperature gas phase equilibrium measurements was a hermetically sealed constant volume system. Butadiene was allowed to expand into the evacuated system to fill the 5-liter calibrated reaction volume to a pre-determined pressure. For this purpose, the flask was connected to the manifold through a side arm in place of one of the ampoules. By chilling a side arm trap on the reaction flask to −195°, the diene was frozen out while the reaction flask was sealed off with a torch. The flask was placed in the furnace and sealed into the system with the magnetically controlled hammer above the breaker seal.

To study the depolymerization, a measured amount of redistilled and degassed vinylcyclohexene was introduced into the side arm trap of the reaction flask using a rubber serum cap and hypodermic syringe and an auxiliary inlet to the side arm trap. Otherwise, the procedure was as above.

The temperature of the furnace was controlled to ±1° by a Brown recording potentiometer. After the reaction period, the breaker seal was ruptured and the contents were rapidly expanded into an ampoule which had been chilled to −195°. Condensation in the manifold was prevented by maintaining the temperature electrically at approx. 130°. The reaction vessel was then sealed off with a torch to isolate the high temperature zone from the system.

Analyses of the products proceeded by conventional low temperature distillation techniques. Gas chromatography was used to check the identity of the products, and the amounts were quantitatively determined by direct weighing or pressure measurements. Some of the run conditions, data and results over the temperature range, 360–430°, are summarized in Table I.

At 400° and higher, some hydrogen and methane in equal amounts, and a liquid product in which cyclohexane, benzene, cyclohexene, ethylbenzene and styrene were identified as well as vinylcyclohexene were obtained. The amounts of butadiene and vinylcyclohexene in these mixtures, as found by chromatographic analyses, were used for the calculation of the equilibrium data.

At no time was carbonization of the reaction vessel observed in this work. With reference to the data which are collected in Table I, certain observations are possible. At 666°K. and reaction times greater than 40 minutes, the experimental ΔF does reach a constant value (*i.e.*, −9.7 ± 0.2

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(1) Abstracted in part from a thesis submitted by M. A. De Crescente in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Rensselaer Polytechnic Institute, June, 1958.

(2) Union Carbide Corporation Fellow in Chemistry, 1956–1958.

(3) D. Rowley and H. Steiner, *Disc. Faraday Soc.*, **10**, 198 (1951).

(4) G. B. Kistiakowsky and W. W. Ransom, *J. Chem. Phys.*, **7**, 723 (1939).

(5) T. F. Doumani, R. F. Deering and H. C. McKinnis, *Ind. Eng. Chem.*, **39**, 89 (1947).

(6) N. E. Duncan and G. J. Janz, *J. Chem. Phys.*, **20**, 1644 (1952).

(7) G. J. Janz, "Estimation of Thermodynamic Properties for Organic Compounds," Academic Press, Inc., New York, N. Y., 1958, p. 115. 122.

TABLE I

BUTADIENE–VINYLCYCLOHEXENE—EQUILIBRIUM EXPERIMENTS

Temp. (°K.)	Input Press. (atm.)	Input Moles	Time (min.)	Recovery (moles × 10^3) C_4H_6	Recovery (moles × 10^3) C_8H_{12}	K_p (× 10^{-3})	$-\Delta F°$ (kcal. mole^{-1})
698	0.930	0.0918	62	8.86	40.8	0.178	8.0
690	.936	.0875	31	2.70	38.8	.498	8.5
688	.975	.0914	30	2.33	41.4	.715	9.0
626	.907	.0935	46	16.2	33.8	.013	3.1
666	.866	.0840	40	3.68	39.7	.262	7.4
666	.939	.0910	81	1.18	25.3	1.77	9.9
669	.923	.0906	60	1.42	31.9	1.55	9.8
666	.927	.0898	70	1.58	26.9	1.04	9.4
668	.613	.0601	70	1.80	16.8	0.513	8.3
667	.639	.0618	90	0.55	15.0	4.84	11.2
670	.647	.0632	90	1.54	16.8	0.696	8.8
667	.654	.0633	91	0.80	15.7	2.36	10.3
626	.932	.0974	180	.56	39.5	13.0	11.8
645	.977	.0978	139	.82	36.5	5.48	11.0
656	.933	.0932	128	.89	25.0	3.14	10.5
676[a]	4.18	.0474	68	.76	41.8	3.69	11.0
658[a]	4.10	.0471	171	1.02	41.0	7.12	11.3
639[a]	3.27	.0401	156	0.59	32.7	7.84	11.4

[a] Depolymerization experiments.

kcal./mole). The experimental ΔF at a constant temperature is independent of the initial pressure of the reactants, although the reproducibility of the results at lower initial pressures is far less satisfactory. In view of the rather small amounts of diene remaining at reaction equilibrium, the greater scatter in the low pressure experiments reflects the limitations of such experimental studies; the agreement is all that could be expected. That the value of ΔF observed is an equilibrium value was demonstrated by the depolymerization experiments in which vinylcyclohexene was used as the initial reactant.

Comparison of the values predicted by the thermodynamic method and the values calculated from reaction rate data leaves little doubt that the present experimental values confirm the thermodynamic values. The fact that reaction equilibrium data can be predicted more accurately by the thermodynamic method where precise data are available than by experimental measurements, especially in the gas phase at moderately high temperatures, is clearly illustrated by these results.

Discussion

The method of group equations[7,8] may be used to estimate the thermodynamic properties for a compound quite precisely providing the thermodynamic properties of the parent compounds are accurately known and the corrections arising from differences in symmetry factors and internal rotations are observed. The free energies of formation for vinylcyclohexene were thus estimated by the group equation

$$\Delta F_f{}^0 \text{ [vinylcyclohexene]} = \Delta F_f{}^0 \text{ [styrene]} + \Delta F_f{}^0 \text{ [cyclohexane–benzene]} + RT \ln 3 \qquad (2)$$

using the data for styrene, cyclohexene and benzene,[8] and where the factor $RT \ln 3$ brings about a balance in the contributions due to the symmetry factors. The hindered internal rotation in vinylcyclohexene was assumed equal to that in styrene in this estimate. The results together with the data for butadiene,[8] and the equilibrium free energy changes for the dimerization reaction

$$2(\text{Butadiene}) \underset{k_r}{\overset{k_f}{\rightleftarrows}} \text{Vinylcyclohexene} \qquad (1)$$

are summarized in Table II. These values are recommended for calculations to those reported by Duncan and Janz[6] since in the earlier work, the more approximate method of group contributions with no corrections for symmetry factors was used (*e.g.*, at 1000°K., the earlier estimate is 2.8 kcal./mole too low).

The values predicted from the rate data (Table II) were calculated from the expressions for the dimerization of butadiene[3]

$$k_f = 1.38 \times 10^{11}\ e^{-(26,800/RT)} \text{ cc. mole}^{-1} \text{ sec.} \quad (690\text{–}925°\text{K.})$$

and the depolymerization of vinylcyclohexene[4]

$$k_r = 2.35 \times 10^8\ e^{-(36,000/RT)} \text{ sec.}^{-1} \quad (783\text{–}977°\text{K.})$$

and the well known relation between the equilibrium and reaction rate constants

$$K_p = \frac{k_f}{2k_r}(RT)^{-1} \qquad (3)$$

where the subscripts refer to the forward and reverse processes (equation 1), R is the gas constant in l.-atm./deg. mole, and the factor 2 refers both rate processes to one gram mole of butadiene in the equilibrium expression. Inspection of the calculations by Duncan and Janz[6] shows that these factors were not taken into account so that the earlier results are of qualitative rather than quantitative significance only.

The experimental results of the present study agree well with the limits of the experimental work with the thermodynamically predicted values for the equilibrium free energy changes. The cause for the disagreement of the results predicted from the reaction velocity studies lies most probably in the expression for the rate of depolymerization of vinylcyclohexene as discussed elsewhere.[6] The frequency factor and activation energy for the depolymerization[5] seem unusually low for homogeneous thermal dissociation processes.

The heat and entropy changes for the dimerization at 25° and 1 atm. are −35.40 kcal. and −43.01 e.u., respectively, as calculated from the recent value for heat of formation of vincylcyclohexene,[9] 17.26 kcal./mole, an estimated value for the entropy of vinylcyclohexene, 90.23 e.u., and the current values for butadiene.[8] The same basic group equation as in the preceding calculations was used for entropy but with the factor from symmetry considerations now $-R \ln 3$. The above value may be compared with the values 89.6, 90.3, 88.3 and 86.7 e.u. as estimated by Kistiakowsky and Ransom[4] using cyclohexane, methylcyclohexane, cyclohexene and ethylcyclohexane as "parents" and the more approximate procedures of simple group contributions.

A comparison of the value of entropy of reaction with the values for the entropies of activation observed experimentally[4] for the dimerization reaction of butadiene at 600°K. is of interest. The entropy of activation $\Delta S^{\ddagger}$ for the dimerization of butadiene, calculated from the value of non-exponential A factor, $10^{9.96 \pm 0.18}$ cm.^{3}/g. mole sec., found in the kinetic measurements[4] at 600°K. is

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[8] F. D. Rossini and Associates, Eds.; "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

[9] F. W. Maron and E. J. Prosen, Nat. Bur. Stds. Report 2037, Washington, D. C., 1952.

TABLE II

THERMODYNAMICS OF THE BUTADIENE–VINYLCYCLOHEXENE EQUILIBRIUM

T (°K.)	298.1	300	400	500	600	700	800	900	1000
			(a) Free energies of formation (kcal./mole)						
Butadiene[a]	36.01	36.07	39.46	43.05	46.78	50.60	54.48	58.40	62.36
Vinylcyclohexene	46.18	46.07	57.20	68.82	80.70	92.76	104.92	117.17	129.43
			(b) Equilibrium free energy changes (kcal./mole)						
Thermodynamic data	−25.84	−26.07	−21.72	−17.28	−12.86	− 8.44	−4.04	0.37	4.71
Reaction rate[b] data	.....	.....	.....	.....	(− 3.2)	(− 1.9)	−0.6	0.7	2.0

[a] See ref. 8. [b] Values in brackets are extrapolated values.

−18.3 e.u. per g. mole per cc. if the transmission coefficient is assumed to be unity. The entropy of reaction ΔS for this process at 600°K. may be computed from the value for butadiene,[8] 84.36 e.u., and vinylcyclohexane, 124.75 e.u., both at 1 atmosphere, using the Sackur Tetrode equation to correct these values to volume concentration units. The above value for vinylcyclohexene was calculated by the method of group equations. This computation gives, as the entropy change for the dimerization of butadiene at 600°K., the value of −21.2 e.u./per cc. per g. mole of butadiene. Whereas the calculations based on statistical thermodynamics for the entropies of activation assuming both linear and a cyclic transition state complexes were not sufficiently free from assumptions to distinguish conclusively between the two possibilities,[10] the close agreement above between the entropy change for the reaction and entropy of activation makes the assumption of a highly circumscribed transition state, rather similar in structure to the product molecule, *i.e.*, cyclic, a very probable one. The question still remains open whether the transition state in this process is a diradical or simply a polarized molecular state.

Acknowledgments.—One of us (G.J.J.) wishes to thank Hervey H. Voge, Emeryville, Calif., and Yukio Mikawa, Tokyo, Japan, for directing attention to the need for revision and correction of the earlier calculations.

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[10] A. Wassermann, *J. Chem. Soc.*, 612 (1942).

VOLUME EFFECTS ON MIXING IN THE LIQUID $Bi-BiI_3$ SYSTEM[1]

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Volume effects on mixing in the liquid $Bi-BiI_3$ system have been determined by measurements of the density as a function of temperature. The total volume of the system decreases on mixing. The partial molar volume of BiI_3 differs only slightly from the molar volume of the pure salt while the partial molar volume of the bismuth is much less than the molar volume of pure bismuth. These volume effects are analogous to the changes found previously for the bismuth–chloride and bismuth–bromide systems and are interpreted in terms of the same model of an interstitial type of solution. The experimental values in all three halide systems are in fair agreement with an expression derived from the model which relates the partial molar volume of the bismuth with the halide ion radius.

Introduction

In an effort to gain some knowledge concerning the nature of metal–salt solutions we have previously studied the volume effects in the $Bi-BiCl_3$ and the $Bi-BiBr_3$ systems.[2] As a continuation of this work we have measured the volume changes in the $Bi-BiI_3$ system. Bismuth has been shown[3] to exhibit appreciable solubility in BiI_3, analogous to the $Bi-BiCl_3$ and $Bi-BiBr_3$ systems. There is some evidence for the formation of solid BiI. In the temperature range 406–500° and up to about 50 mole % bismuth, one liquid phase is obtained. Solutions of $Bi-BiI_3$ in this range have been investigated in the present study.

Experimental

As in the previous experiments, the densities of the liquid $Bi-BiI_3$ mixtures were determined by a pycnometric method. In general, the procedures were the same as those used for the chloride and bromide experiments.[2]

The BiI_3 was prepared by reaction of reagent grade Bi_2O_3 with aqueous HI followed by evaporation of the water under a nitrogen stream. The crude BiI_3 thus obtained was distilled twice under a stream of dry N_2. The product from the second distillation was ground in a mortar and stored in a desiccator. Two separate preparations of BiI_3 were made. They gave bismuth analyses of 35.32 and 35.20% compared to the theoretical amount for bismuth of 35.44%. As it had previously been found in vapor pressure measurements on the $Bi-BiI_3$ system[4] that BiI_3 tends to decompose to yield free I_2 when heated, it was thought that a small amount of free I_2 might be present in the distilled BiI_3. To test for the presence of any free I_2, duplicate samples of BiI_3 were dissolved under a nitrogen atmosphere in oxygen-free KI solution acidified with HCl and immediately titrated with $Na_2S_2O_3$ solution. The results showed less than 0.03% I_2 to be present in the BiI_3. The melting point of the BiI_3 used ranged from 405.9 to 406.6°.[4]

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[1] This work was made possible by the financial support of the Research Division of the United States Atomic Energy Commission.

[2] F. J. Keneshea, Jr., and D. Cubicciotti, THIS JOURNAL, **62**, 843 (1958); **63**, 1112 (1959).

[3] (a) L. Marino and R. Becarelli, *Atti Accad. Lincei*, **21** [5], 695 (1912); (b) H. S. Van Klooster, *Z. anorg. Chem.*, **80**, 104 (1913); (c) G. G. Urazov and M. A. Sokolova, *Akad. Nauk. SSSR., Inst. Obshch. Neorg. Khim., Sektor Fiz-Khim. Anal., Izvest.*, **25**, 117 (1954).

[4] D. Cubicciotti and F. J. Keneshea, Jr., THIS JOURNAL, **63**, 295 (1959).