82. *The Mechanism of Additions to Double Bonds. Part VII. Chemical Equilibrium in Solution and in the Gaseous State.*

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The constants of two association equilibria, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ and $2C_5H_6 \rightleftharpoons C_{10}H_{12}$(di*cyclo*pentadiene *) are compared in the gas phase and in solution by using van 't Hoff's equation involving the solubilities of the reactants and of the products. It is shown that the heat changes of both gaseous associations are not much altered by the presence of the solvent, and also that the statistical weight of ethane is of the same order of magnitude in both states. The statistical weight of di*cyclo*pentadiene is somewhat larger in solution than in the gas phase.

THE constant, K_s, of a chemical equilibrium a + b $\rightleftharpoons$ c in solution is connected with K_g, the constant of the same equilibrium in the gas phase, by

$$K_s = K_g S_c / S_a S_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(see van 't Hoff, " Lectures on Theoretical and Physical Chemistry," 1898, Vol. I, p. 221;

* Di*cyclo*pentadiene exists in two geometrical isomeric forms. The experiments described in this and in the following papers deal with the *endo*-form only (for formula, see following paper, p. 372).

Dimroth, *Annalen*, 1910, **377**, 134), where S_a, S_b, and S_c are the solubilities of the reactants and of the product. The equilibrium constants and the solubilities are defined by

$$K = (\text{Vol. concn. of c})/(\text{Vol. concn. of a})(\text{Vol. concn. of b}) \quad . \quad . \quad . \quad (2)$$
$$S = (\text{Vol. concn. in soltn.})/(\text{Vol. concn. in gas}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and both expressions can be represented by products of exponential and non-exponential factors, thus :

$$K_g = B_g e^{-H_g/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$
$$K_s = B_s e^{-H_s/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$
$$S = C e^{-\lambda/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In these expressions H_g and H_s are the total heat changes of the chemical equilibrium in the gas phase and in solution, respectively, and λ is the total heat of solution. The total heat change of the gaseous equilibrium is given by

$$H_g = RT^2 \mathrm{d} \ln K_g/\mathrm{d}T - RT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and for sufficiently dilute solutions we have (cf. Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 613; Bell, *ibid.*, p. 436)

$$H_s = RT^2 \mathrm{d} \ln K_s/\mathrm{d}T - RT^2\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$
$$\lambda = RT^2 \mathrm{d} \ln S/\mathrm{d}T + RT^2\alpha - RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where α denotes the coefficient of thermal expansion of the solvent.

The non-exponential factors B_g and B_s in (4) and (5) are a measure of the statistical weight of the product of the chemical reaction, and the non-exponential factor C in (6) is a measure of the statistical weight of the molecules in the condensed state. For the sake of brevity the factor C is hereinafter called the " weight factor."

If the chemical equilibrium constants and solubilities in (1) are expressed by (5), (4), and (6), then the following relationships between the exponential and the non-exponential factors are obtained :

$$H_s - H_g = \lambda_c - \lambda_a - \lambda_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$
$$B_s/B_g = C_c/C_a \times C_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where the subscripts s and g refer to the solution and to the gas phase respectively, and the subscripts a, b, and c refer to the reactants and to the reaction product. It will be seen that the heat changes and the B factors of the chemical equilibrium in solution can be compared with the corresponding quantities in the gas phase if the heats of solution and the weight factors are known.

Results and Discussion.—Equations (10) and (11) have been used to compare the two parameters of the constants of the two association equilibria shown on p. **367**. Horiuti (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **17**, 222) has carried out accurate solubility determinations of ethylene, hydrogen, and ethane in the five solvents shown in cols. 2—6 in Table I, and we have determined the solubilities of gaseous *cyclo*pentadiene and di*cyclo*pentadiene in paraffin. The logarithms of the solubilities are, in the temperature range given in col. 8 of Table I, linear functions of the reciprocal absolute temperature, and as the coefficients of the thermal expansion of the solvents are also known, the heats of solution λ, and the weight factors, C, can be obtained by using the equations (9) and (6). In this and in the following papers we have conventionally chosen the sign of all the heat and energy changes to be positive if heat is absorbed. All the λ values and the figures in the penultimate line of the table are given in kg.-cals. per g.-mol.

The figures in the penultimate line have been obtained by introducing the heats of solution into equation (10). The formation of ethane is more exothermic in solution than in the gas phase because the dissolution of both ethylene and ethane is exothermic and the heats of solution are similar, whereas the dissolution of hydrogen is an endothermic process. The formation of di*cyclo*pentadiene, on the other hand, is more exothermic in the gas phase because the process of solution of two *cyclo*pentadiene molecules is more exothermic than that of one di*cyclo*pentadiene molecule. The observed differences between

H_s and H_g do not exceed 1·6 kg.-cals., and this is, at the most, 10% of the values of H_g, which is about — 32·5 kg.-cals. for the reaction between ethylene and hydrogen (cf. references given by Teller and Topley, J., 1935, 876), and about — 19 kg.-cals. for the association of *cyclo*pentadiene.

TABLE I.

	CCl_4.	C_6H_6.	PhCl.	$COMe_2$.	$CH_3{\cdot}CO_2Me$.	Paraffin.	Approx. temp. range.
λ_{H_2}	+1·22	+1·50	+1·22	+1·22	+1·22	—	−60 to 50° *
$-\log_{10} C_{H_2}$	0·19	0·04	0·32	0·11	0·14	—	
$\lambda_{C_2H_4}$	−2·10	−1·96	−2·21	−1·89	−1·98	—	5—45 †
$-\log_{10} C_{C_2H_4}$	0·96	0·89	1·16	0·82	0·85	—	
$\lambda_{C_2H_4}$	−2·48	−2·01	−2·32	−1·97	−1·98	—	5—45
$-\log_{10} C_{C_2H_6}$	1·09	0·89	1·15	0·92	0·92	—	
$\lambda_{C_5H_6}$	—	—	—	—	—	−7·5±0·2	27—73
$-\log_{10} C_{C_5H_6}$	—	—	—	—	—	3·1±0·1	
$\lambda_{C_{10}H_{12}}$	—	—	—	—	—	−13·5±0·3	55—111
$-\log_{10} C_{C_{10}H_{12}}$	—	—	—	—	—	4·9±0·2	
$H_s - H_g$	−1·60	−1·55	−1·33	−1·30	−1·22	+1·5±0·7	—
$\log_{10} B_s - \log_{10} B_g$	0·08	0·08	0·32	0·00	0·08	1·3±0·4	—

* In carbon tetrachloride and benzene, 0—59° and 7—63° respectively.
† In chlorobenzene, 0—90°.

The figures in the last line of Table I have been obtained by introducing the weight factors, C, into equation (11). The non-exponential factor of the equilibrium between ethane and ethylene and hydrogen is not much changed by the presence of solvents, whereas that of the equilibrium between *cyclo*pentadiene and its dimeride is at least 8 times larger in paraffin than in the gas phase, and the most probable value for $B_{\text{paraffin}} : B_g$ is about 20. The weight factors of hydrogen, ethylene, and ethane are considerably larger than those of *cyclo*pentadiene and di*cyclo*pentadiene, which are 8×10^{-4} and 1×10^{-5} respectively. It is probable also that in the case of other associations the non-exponential factor of the constant of the chemical equilibrium will be of the same order of magnitude in the two states, if the weight factors of the reactants and of the product are not much smaller than unity. If, however, they are much smaller than unity then, in some cases, a considerable solvent influence might be operative. The order of magnitude of this solvent effect cannot be estimated by assuming that the weight factor of the reactants and that of the product are equal. If this assumption had been made in the case of the association of *cyclo*pentadiene, then the estimated value of $B_{\text{paraffin}} : B_g$ would be about 10^3 times larger than the experimental figure.

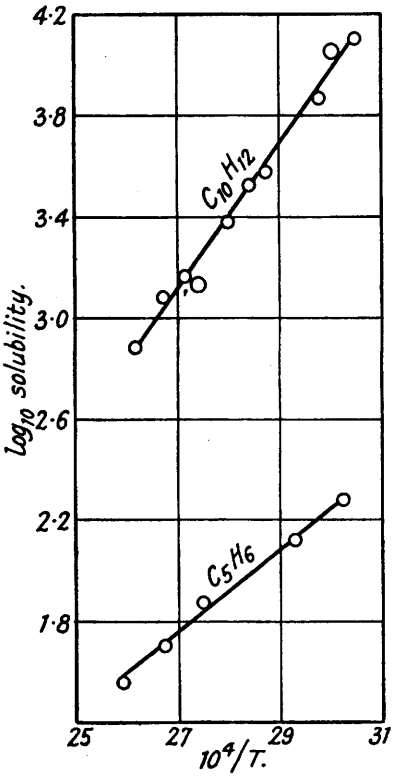
Conclusion.—The constants of two association equilibria involving (*a*) hydrogen and simple hydrocarbons and (*b*) polyatomic molecules have been compared in the gas phase and in solution by using a relationship between solubilities and equilibrium constants in two states. The reactants and the product of equilibrium (*a*) are characterised by numerically smaller heats of solution and larger weight factors than the molecules of association (*b*). The heat change of both gaseous associations is not much altered by the presence of solvents, and also the non-exponential factor of equilibrium (*a*) is of the same order of magnitude in both states. The non-exponential factor of equilibrium (*b*) is about 20 times larger in solution than in the gas phase, but if the weight factors, C, of the reactants and of the products agreed, the non-exponential factor of equilibrium (*b*) would be about 10^3 times larger in the condensed state.

EXPERIMENTAL.

Three samples of di*cyclo*pentadiene were used, the vapour pressures of which agreed within the limits of the experimental error. (1) and (2) : A commercial sample (Light, London) was redistilled at 20 mm. twice and three times respectively. (3) *cyclo*Pentadiene was twice redistilled in the apparatus mentioned in Part I (*loc. cit.*), and then kept for 4 months at about 20° in a vacuum; the product thus obtained was redistilled at 20 mm. in a stream of nitrogen. The following densities were determined at 57°, 66°, 78° and 100° respectively: 0·950, 0·942, 0·925, 0·888. The b. p.'s, m. p.'s, and refractive indices of the di*cyclo*pentadiene samples agreed with the values in the literature. Both di*cyclo*pentadiene and *cyclo*pentadiene were dissolved in paraffin shortly after the final distillation. Two samples of paraffin (B.P.) were used

and both had $d_4^{21°}$ 0·8820, $n_D^{21°}$ 1·4818 and a coefficient of thermal expansion of $6·4 \times 10^{-4}$ per degree as determined in the temperature range 27—170°. Neither sample had a measurable bromine consumption. The vapour pressure of sample (1) at 62·3°, 73·9°, 83·4°, 95·4°, 102·0° and 111° was 0·2, 0·5, 1·0, 2·0, 3·0 and 5·0 mm. respectively. The vapour pressure of sample (2) was below 1 mm. at 111°.

The solubilities were measured in the apparatus represented in Fig. 2 of the preceding paper. The *cyclo*pentadiene or the di*cyclo*pentadiene solution was pipetted into bulb B_2 which was first cooled to — 80° while the whole apparatus was thoroughly evacuated. Then B_2 and the part of the apparatus from *f* to *g* and to *h* was brought to the thermostat temperature by covering B_2 with the helical jacket and by pumping oil through the metal tubing. The oil temperature was measured with standardised thermometers, (*a*) in the thermostat and (*b*) and (*c*) at the inlet and at the outlet of the helical jacket, and it was found that the temperature differences between (*a*) and (*b*) and between (*a*) and (*c*) were never greater than 0·1° and 0·5° respectively; the temperatures given below are the means of the three.



The equilibrium concentrations in the gas phase were deduced from the equilibrium pressures, vapour pressures and fugacities being assumed equal. In the experiments involving di*cyclo*pentadiene and sample 1 of the paraffin, the partial vapour pressure of the paraffin was subtracted from the observed total vapour pressure. As the correction is only small, the partial vapour pressure could be calculated from the vapour pressure of pure paraffin on the assumption that Raoult's law is obeyed. In all the other experiments the partial vapour pressure of paraffin could be neglected.

During the measurements, tap T_4 remained closed and the vapour pressure was observed at manometer *M*. In order to attain the equilibrium pressures within 30—60 minutes it was necessary to introduce into bulb B_2 either several pieces of porous porcelain or a small piece of iron and to stir by using a magnet.

In carrying out the experiments involving *cyclo*pentadiene, tap T_3 was closed after the attainment of the equilibrium pressure, the *cyclo*pentadiene vapour outside T_3 was removed, the contents of B_2 were cooled to room temperature, and then the equilibrium concentration of *cyclo*pentadiene in solution was determined by using the method described in Part IV (J., 1936, 1032; cf. also Khambata, Thesis, London, 1938, p. 85). In some experiments the contents of B_2 were first cooled to — 80° and then the equilibrium solution was brought to room temperature. The thermal expansion of the equilibrium solution between room temperature and the temperature of the solubility determination was determined in separate experiments and found to agree with the thermal expansion of the solvent.

The equilibrium concentration of di*cyclo*pentadiene in paraffin was deduced from $(g_t - g_g)/(V_0 - g_g/d)$; g_t is the total amount of di*cyclo*pentadiene introduced into bulb B_2 at the beginning of the experiments, g_g is the amount of di*cyclo*pentadiene in the gas phase after the attainment of equilibrium, V_0 is the volume of the di*cyclo*pentadiene solution at zero time, and *d* is the density of liquid di*cyclo*pentadiene at the temperature of the solubility determination. g_g can be deduced from the observed equilibrium pressure and the known volume of the apparatus, and *d* can be calculated from the figures given above. In all the experiments V_0 was much greater than g_g/d, and hence correct values for the equilibrium concentration will be obtained, even if the difference between the partial molal volume of di*cyclo*pentadiene in paraffin and the volume of pure liquid di*cyclo*pentadiene should be rather large. Di*cyclo*pentadiene decomposes at elevated temperatures into *cyclo*pentadiene, but under the conditions of the solubility determinations the rate of the decomposition is too slow to affect the accuracy of the results.

Typical Experiments.—15 Cm.³ of an approximately 3M-solution of *cyclo*pentadiene in paraffin were pipetted into bulb B_2, and the equilibrium pressure observed at 54·5° ± 0·2° was

124·0 ± 0·3 mm. 2·00 Cm.³ of the equilibrium solution were added to 0·4457 g. of benzoquinone and made up with benzene to 25·0 cm.³. After all the *cyclo*pentadiene was used, the benzoquinone solution was found to be 0·129 ± 0·001M. Hence the equilibrium solution is 0·450 ± 0·012M, and the solubility of gaseous *cyclo*pentadiene in paraffin is 74 ± 3. 15·0 Cm.³ of a 3·00M-solution of di*cyclo*pentadiene in paraffin (sample 1) were pipetted at 20° into bulb B_2. At 83·7° ± 0·2° the total equilibrium pressure was 23·1 ± 0·2 mm., the calculated partial vapour pressure of the paraffin 0·8 mm., the amount of di*cyclo*pentadiene in the gas phase 0·17 g., and its density 0·915. The thermal expansion of the 3·00M-solution was determined in a separate experiment, and thus it was found that V_0 was 16·57 cm.³. From these data it follows that, at equilibrium, the di*cyclo*pentadiene solution was 2·46 ± 0·03M, and hence the solubility of gaseous di*cyclo*pentadiene in paraffin is 2·50 ± 0·06 × 10^3.

The results of all the solubility measurements are in Table II and in the figure.

TABLE II.

Solubilities of Gaseous cyclo*Pentadiene and Di*cyclo*pentadiene in Paraffin.*

Temp.	Total equilm. press., mm.	Equilm. concn. in soln., g.-mol./l.	$\log_{10}S$.	Temp.	Total equilm. press., mm.	Equilm. concn. in soln., g.-mol./l.	$\log_{10}S$.
			*cyclo*Pentadiene.				
26·5°	79·3	0·719	2·23±0·02	54·5°	124·0	0·450	1·87±0·03
34·9	33·5	0·219	2·10±0·02	63·5	110·0	0·262	1·70±0·07
34·9	85·8	0·537	2·08±0·04	73·2	143·0	0·244	1·57±0·02
35·2	208·0	1·48	2·14±0·02				
			Di*cyclo*pentadiene.				
55·1	2·5	1·54	4·10±0·07	91·5	13·5	0·693	3·07±0·04
53·8	4·1	2·67	4·13±0·04	92·2	35·0	2·39	3·19±0·04
54·8	4·4	2·78	4·11±0·06	94·3	13·0	0·618	3·09±0·05
59·0	5·3	2·99	4·07±0·05	95·0	15·5	0·845	3·08±0·05
62·3	8·0	2·73	3·86±0·03	95·0	18·0	1·18	3·22±0·05
73·9	15·0	2·58	3·58±0·02	95·5	32·9	2·34	3·22±0·05
78·7	9·1	1·35	3·51±0·04	102·1	44·5	2·21	3·09±0·02
83·7	23·1	2·46	3·39±0·01	111·0	75·7	2·46	2·89±0·03
92·2	7·0	0·371	3·08±0·05				

The integration of equation (9) was carried out by using the above data and the coefficient of thermal expansion given on p. 370.

It is deduced in the following communication that the heat change of the equilibrium between *cyclo*pentadiene and di*cyclo*pentadiene is 17·3 ± 0·6 kg.-cals. in paraffin solution. By substituting this value and the heats of solution of *cyclo*pentadiene and di*cyclo*pentadiene in equation (10) the heat change in the gas phase can be calculated.

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