136. *Kinetics of a Diene Association under Constant Volume Conditions.*

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The velocity coefficient, k, of the bimolecular association of *cyclo*pentadiene can be represented by $k = A_v e^{-E_v/RT}$ or by $k = A_p e^{-E_p/RT}$ where E is the activation energy and the subscripts indicate that the two parameters refer to constant volume or to constant pressure respectively. In this paper the activation energy, E_v, and the non-exponential factor, A_v, relating to the association of pure liquid *cyclo*pentadiene are calculated and compared with the corresponding quantities of the gaseous reaction. It is pointed out that in contrast to A_p and E_p, which increase with increasing pressure, A_v and E_v are independent of the pressure within the experimentally investigated range.

It is of interest to calculate the activation energy, E, and the non-exponential A factor of the Arrhenius equation for homogeneous bimolecular associations, under constant volume conditions, both in the condensed and in the gaseous state. The results of the experiments now to be discussed make this possible for the first time.

The reaction investigated is the dimerisation of *cyclo*pentadiene to produce *endo*-di*cyclo*pentadiene. In previous work the E and A values for the formation of gaseous *endo*-di*cyclo*pentadiene were determined at constant volume (Benford, Khambata, and Wassermann, *Nature*, 1937, **139**, 669; Benford and Wassermann, J., 1939, 362; Schulze, *Oel und Kohle*, 1938, No. 6, 113; compare also Koenig, Diss., Berlin. For a discussion of the results of Harkness, Kistiakowsky, and Mears, *J. Chem. Physics*, 1937, **5**, 682, see J., 1939, 364, 384), but the kinetic measurements in the condensed phase were carried out at constant pressure (Wassermann, J., 1936, 1029; Khambata and Wassermann, J., 1939, 374; Benford, Kaufmann, Khambata, and Wassermann, *ibid.*, p. 381; Kaufmann and Wassermann, *ibid.*, p. 870; Raistrick, Sapiro, and Newitt, *ibid.*, p. 1761). In this paper the activation energy of the association of pure liquid *cyclo*pentadiene is deduced from

$$E_v = E_p + \boldsymbol{R}T^2\alpha_p\gamma/\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here E_v and E_p, the " activation energies " relating to constant volume and constant pressure respectively, can be defined, for the present purpose, by $\boldsymbol{R}T^2(\partial \log k/\partial T)_v$ and by $\boldsymbol{R}T^2(\partial \log k/\partial T)_p$ where k is the bimolecular velocity coefficient; α_p, the coefficient of thermal expansion of *cyclo*pentadiene, at pressure P, is $(\partial \log v/\partial T)_p$; β, the compressibility of *cyclo*pentadiene (the sign of which is positive in the present case) is $(\partial \log v/\partial p)_p$ and γ is $(\partial \log k/\partial p)_T$. Numerical values of the latter quantities were calculated from the data given by Raistrick, Sapiro, and Newitt (*loc. cit.*) and are listed below :

Data for the Calculation of the Activation Energy E_v *of the Association of Pure Liquid* cyclo*Pentadiene.*

	$10^3\alpha_p$ (deg.$^{-1}$).			$10^5\beta$ (atm.$^{-1}$).	$10^4\gamma$ (atm.$^{-1}$).	Pressure range (in atm.) for calculation of	
Temp.	1 Atm.	1000 Atm.	3000 Atm.			β.	γ.
40°	1·43	0·67	0·95	5·80	4·41	1000—2500	1—2500
30	1·40	0·89	0·86	5·10	4·03	1000—3500	1—3500
20	1·37	1·0	0·58	4·61	3·76	1000—3500	1—4000
0	1·23	1·2	0·48	3·4	3·60	1000—4000	1—5000

In general, the coefficients of thermal expansion, the compressibilities, and γ will be functions of the pressure,* but in the association of *cyclo*pentadiene only the coefficient of thermal expansion is markedly influenced by pressure changes, while the compressibilities at 40°, 30°, and 20° are independent of the pressure within the range given in col. 7, and γ is independent of the pressure within the whole experimentally investigated range given in col. 8. For these reasons, coefficients of thermal expansion relating to 1, 1000, and 3000 atm. but only one compressibility and one γ value have been computed for each of the four temperatures at which the kinetic measurements were carried out.

The foregoing data were used to calculate 12 values in the first three columns of the next table, each set of figures being obtained by using the coefficient of thermal expansion at 1, 1000, and 3000 atm., respectively. In order to deduce the activation energy E_v (col. 5), the mean values of these sets of figures and the activation energies, E_p, relating to 1, 1000, and 3000 atm. were substituted in (1). The A factors in the last two columns were obtained from the relevant activation energies and velocity coefficients by using the Arrhenius equations

$$k = A_p e^{-E_p/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$k = A_v e^{-E_v/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In carrying out these calculations the activation energies and velocity coefficients at atmospheric pressure were obtained from the mean values of the figures given by Benford, Kaufmann, Khambata, and Wassermann (*loc. cit.*) and Raistrick, Sapiro, and Newitt (*loc. cit.*), while the E and k values relating to 1000 and 3000 atm. were taken from the latter authors.

Kinetics of the Association of Pure Liquid cyclo*Pentadiene.*

$\boldsymbol{R}T^2\alpha_p\gamma/\beta$ (kg.-cals.).					$\log_{10} A_p$.	$\log_{10} A_v$.
α (1 atm.).	α (1000 atm.).	α (3000 atm.).	E_p (kg.-cals.).	E_v (kg.-cals.).	(A = l.g.-mol.$^{-1}$ sec.$^{-1}$.)	
4·3	1·0	1·4	16·6 ± 0·4 (1 atm.)	20·7 ± 0·7	6·1 ± 0·3 (1 atm.)	9·2 ± 0·5
4·6	1·2	1·2	17·7 ± 0·4 (1000 atm.)	19·1 ± 0·8	7·4 ± 0·3 (1000 atm.)	8·1 ± 0·5
4·4	1·4	0·8	18·6 ± 0·4 (3000 atm.)	19·7 ± 0·7	8·8 ± 0·3 (3000 atm.)	8·8 ± 0·6
4·0	1·8	0·8				

These figures show that in contrast to E_p and A_p, which increase markedly with

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* An example of this is the reaction between pyridine and ethyl iodide in acetone solution (Gibson, Fawcett, and Perrin, *Proc. Roy. Soc.*, 1935, *A*, **150**, 233).

increasing pressure, the pressure dependence of the activation energies E_v and of A_v is smaller than the experimental error. It follows, therefore, that

$$E_p \text{ (pure liquid state)} - E_v \text{ (gas)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$A_p \text{ (pure liquid state)}/A_v \text{ (gas)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

are functions of the pressure, whereas

$$E_v \text{ (pure liquid state)} - E_v \text{ (gas)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$A_v \text{ (pure liquid state)}/A_v \text{ (gas)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

are independent of the pressure within the limits of the experimental error and the range referred to in the first table. It is believed, therefore, that the parameters of (3) are more characteristic of the kinetics in the condensed state than those of (2), and for this reason numerical values of (6) and (7) are of interest. [The numerical values of (4) and (5) have been discussed in the previous work (*loc. cit.*); cf. also Wassermann, *Trans. Faraday Soc.*, 1938, **34**, 128.] The figures in the second table and the results of Benford and Wassermann (*loc. cit.*) being used, it follows that (6) amounts to 3·2 ± 1·3 kg.-cals. and the ratio (7) is at least 40, the most probable value being 400.

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