184. *The Mechanism of Addition to Double Bonds. Part X. Kinetics of Association of* cyclo*Pentadiene.*

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The velocity coefficients of the bimolecular association of *cyclo*pentadiene have been measured in three polar solvents and it has been found that the parameters of the Arrhenius equation, $k = Ae^{-E/RT}$, are similar to those in non-polar solvents and in the gas phase. Hence, the energies of solution of two *cyclo*pentadiene molecules and of the gaseous transition state are approximately equal, and the collision number in the various solvents is of the same order of magnitude as that in the gaseous phase.

It is of interest for the theories of solvent effects in chemical kinetics to compare the rate of one and the same homogeneous, bimolecular reaction in polar and in non-polar solvents and in the gas phase. The results of experiments described in this paper and in previous communications (J., 1936, 1028; this vol., pp. 362, 371, 381) enable such a comparison to be made.

The reaction investigated is the diene association, 2 *cyclo*pentadiene = di*cyclo*pentadiene. Velocity coefficients, *k*, of experiments at various temperatures are in Table I.

TABLE I.

Solvent.	Temp.	Initial concn. of C_5H_6 (g.-mol./l.).	$k \times 10^4$ (l./g.-mol. min.).	Solvent.	Temp.	Initial concn. of C_5H_6 (g.-mol./l.).	$k \times 10^4$ (l./g.-mol. min.).
$CH_3 \cdot CO_2H$	25·0°	1·311	1·2	EtOH	0°	2·675	0·17
	25·0	1·311	1·2		0	2·627	0·17
	25·0	0·583	1·3		25·0	2·386	1·5
	35·2	1·935	2·1		35·0	1·927	5·3
	53·1	1·283	10·0		55·0	2·107	16
	70·0	0·501	50·0	$Ph \cdot NO_2$	0	2·423	0·13
CS_2	0	2·820	0·078		0	1·820	0·13
	22·0	2·930	0·71		25·0	1·908	1·2
	35·1	2·460	2·4		35·1	1·766	3·0
					55·0	1·632	16

The technique of the measurements was the same as that described in the previous work (*locc. cit.*). In acetic acid, the second-order velocity coefficients decrease in each run, probably owing to the reverse reaction or to a consecutive reaction; therefore the first six *k* values were obtained by extrapolating the observed velocity coefficients to zero time. In the other solvents recorded in Table I the association was of the second order and the *k* values are the means of the observed velocity constants.

The activation energies, *E*, the velocity coefficients at 20° and the non-exponential *A* factors of the Arrhenius equation are in Table II, which also contains the temperature range and the number of temperatures at which the experiments have been carried out.

TABLE II.

Measurements in:	$CH_3 \cdot CO_2H$.	EtOH.	$Ph \cdot NO_2$.	CS_2.	C_6H_6.	CCl_4.	C_5H_6.*	Paraffin.	Gas.
E (kg.-cals.)	14·7 ± 1	16·4 ± 0·8	15·1 ± 0·4	16·9 ± 0·5	16·4 ± 0·6	17·1 ± 0·4	16·2 ± 0·8	17·4 ± 0·3	16·7 ± 0·6
$k_{20^\circ} \times 10^7$ (l./g.-mol. sec.)	10 †	19	13	9·3	6·6	7·9	5·6 †	9·8	—
$\log_{10} A$ (A = l./g.-mol. sec.)	5·0 ± 0·7	6·4 ± 0·6	5·5 ± 0·3	6·2 ± 0·3	6·1 ± 0·4	6·7 ± 0·3	5·8 ± 0·5	7·1 ± 0·2	6·1 ± 0·4
Temp. range	25—70°	0—55°	0—55°	0—35°	15—55°	0—55°	−2 to 80°	−1 to 172°	79—150°
No. of temps.	4	4	4	3	5	5	10	7	9

* *cyclo*Pentadiene. † Extrapolated to zero time.

Evans and Polanyi (*Trans. Faraday Soc.*, 1935, **31**, 890) and Wynne-Jones and Eyring (*J. Chem. Physics*, 1935, **3**, 492) deduced an equation which can be written in the form $E_{\text{soln.}} - E_{\text{gas}} = \lambda_{\text{initial state}} - \lambda_{\text{transition state}}$, where the λ's are the energies of solution. The data in Table II show that the activation energies in the polar and the non-polar solvents and in the gaseous state are approximately equal, and, therefore, the energies of solution of two gaseous *cyclo*pentadiene molecules and of the *cyclo*pentadiene–*cyclo*pentadiene transition state must be similar (cf. Wassermann, *Trans. Faraday Soc.*, 1938, **34**, 128). The figures in ll. 3 and 4 of Table II show that the velocity coefficients and the kinetic *A* factors also are not markedly changed by the medium. The *A* values are products of steric factors and bimolecular collision numbers. If it is assumed that the steric factors in the two states are equal (cf. *Trans. Faraday Soc.*, 1938, *loc. cit.*), it can be concluded that the collision number in polar solvents, in non-polar solvents, and in the gas phase is of the same order of magnitude.

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