The product of the ,dehydrochlorination was isolated by refluxing the mixtures of the above components for 8 hours, followed by distillation of the solvent mixtures. The product was then recrystallized three times using absolute ethanol. The product has a m.p of 80°C, The elemental analysis shown in table (2) as well as the infrared spectrum of the authentic sample shown in Fig. (3) demonstrated that" the olefin 1,1-dichloro-2,2-diphenylethylene is the product formed in the reaction.

B- results and discussion

1) Reaction Mechanism and Rate constant Calculations:-

The reaction rate of the dehydrochlorination of 1,1,1-trichloro-2,2-diarylethanes [1,1,1-trichloro-2,2-diphenylethane, 1,1,1-trichloro-2,2-bis-p-chlorophenylethane or 1,1,1-trichlora-2,2-bis-p-methylphenylethane] in the presence of methoxide were found to be frist order with respect to the 1,1,1-trichloro-2,2-diarylethane compound or base.

Mclennan et. al.(51-57) suggested that the dehydrochlorination reaction of 1,1,1-trichloro-2,2-diarylethane derivatives in alcoholic solvents, using base induced medium

$$Ar_2CHCC1_3 + B \longrightarrow Ar_2C{=}CC1_2 + Cl + BH \qquad (13)$$

proceed according to a ElcB mechanism in which the rate determining step is carbanion formation by simple proton transfer:

$$Ar_2CHCC1_3 + \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad Ar_2CCC1_3 + BH \qquad (14)$$

Table . 2 . elemental analysis of 1,1-dichloro-2,2diphenylethane

[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]
[illegible]		[illegible]	[illegible]
		[illegible]	[illegible]

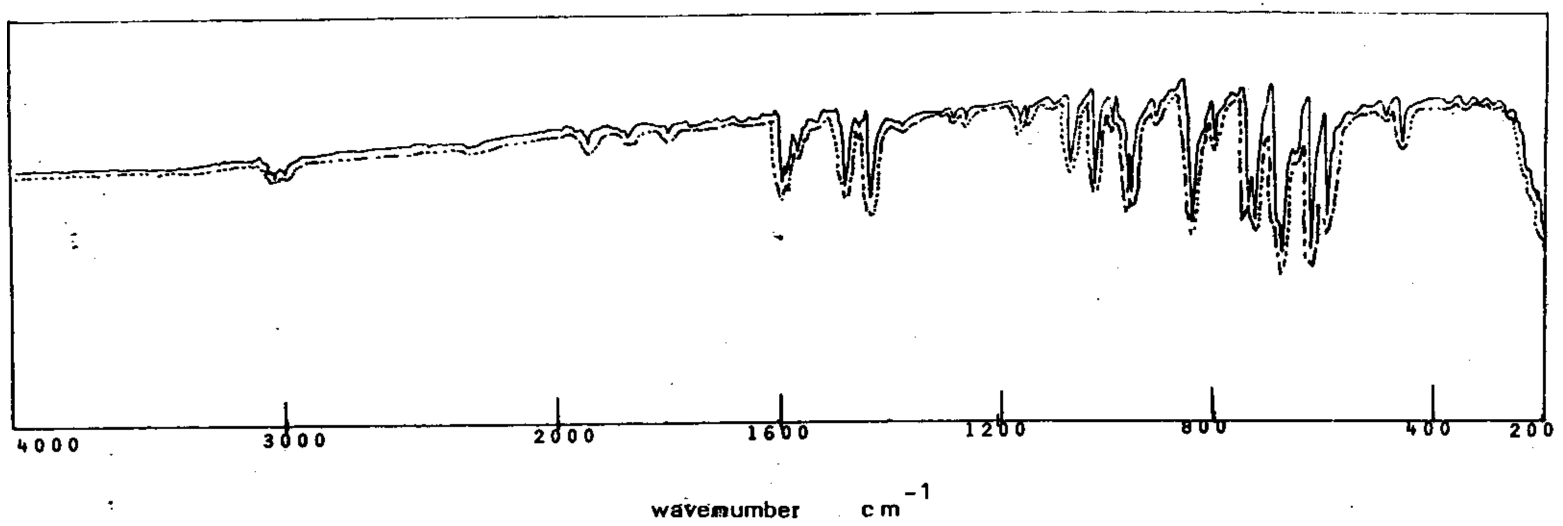

Fig. 3 . Infrared spectrum of 1,1-dichloro-2,2-diphenylethylene

This is followed by a fast step of loosing chloride ion:

$$Ar_2CCC1_3 \xrightarrow{'k_2} Ar_2C=CCI_2 \qquad (15)$$

This mechaism differs from the more usual bimolecular E_2 mechanism, in which the elimination of HCl is a stepwise process, involving an intermediacy of a discrete carbanion$^{(58)}$.

$$Ar_2CHCC1_3 + \quad Ar_2 \underset{CI}{\overset{Cl}{—C1}}-4\ BH + Ar_2CzCC1_2 + \qquad (16)$$

By assuming a steady - state carbanion concentration in the carbanion mechanism we obtain.

$$\text{rate} = \frac{k_1 k_2 [\ Ar_2CHCC1_3\ ] [}{k_{-1}\ [\ BH \quad + k_2}$$

So that second - order kinetic : rate = k_{obs} [Ar_2CHCCI_3] [B ,as will be exhibited by all non - solvolytic E_2 reactions , will be observed under the following conditions (assuming that [Ar_2CHCCI_3] and [B] are comparable) :

0 The frist step (eq. 14) is rate - determining , being essentially the bimolecular , irreversible formation of carbanion , and the second step (eq. 15) is the relatively rapid ejection of the leaving group from the a -carbon atom ($K_2 >> K_{-1}$ [BH]) according to current terminology concerned with elimination

reactions , the leaving group departs from a -carbon atom , and proton is removed from the $ -carbon atom.

ii) The frist step (eq. 14) is a rapidly attained equilibrium and the second (eq. 15) is the rate limiting , unimolecular decomposition of carbanion (K_1 BH >> K_2) . If in this case the base B is not the lyate ion of the solvent , its conjugate acid , BH , must be present in excess to allow the observation of second - order kinetics.

Equal concentration of the substrates and the methoxide ions have been used for determining the specific rate constant (k) , which have been calculated by using the following equation[2] '

$$k_2 - \frac{1}{t}\, a(a-x) \qquad (17)$$

where (x) is the number of moles /1i-ter reacted in time (t) and (a) is the initial concentration of the reactants.

The reaction rate constants corresponding to the different temperatures were evaluated graphically from the slopes "of the stright lines obtained by plotting (1/a - x) aganist (t). All the results of this work has been given in the Appendix (1-3) and only typical results are given in the appropriate places . Typical plots of kinetics of the dehydrochlorination of the investigated compounds are shown in Figures (4-6) . The calculated rate constants for the dehydrochlorination in methanol / carbon tetrachloride

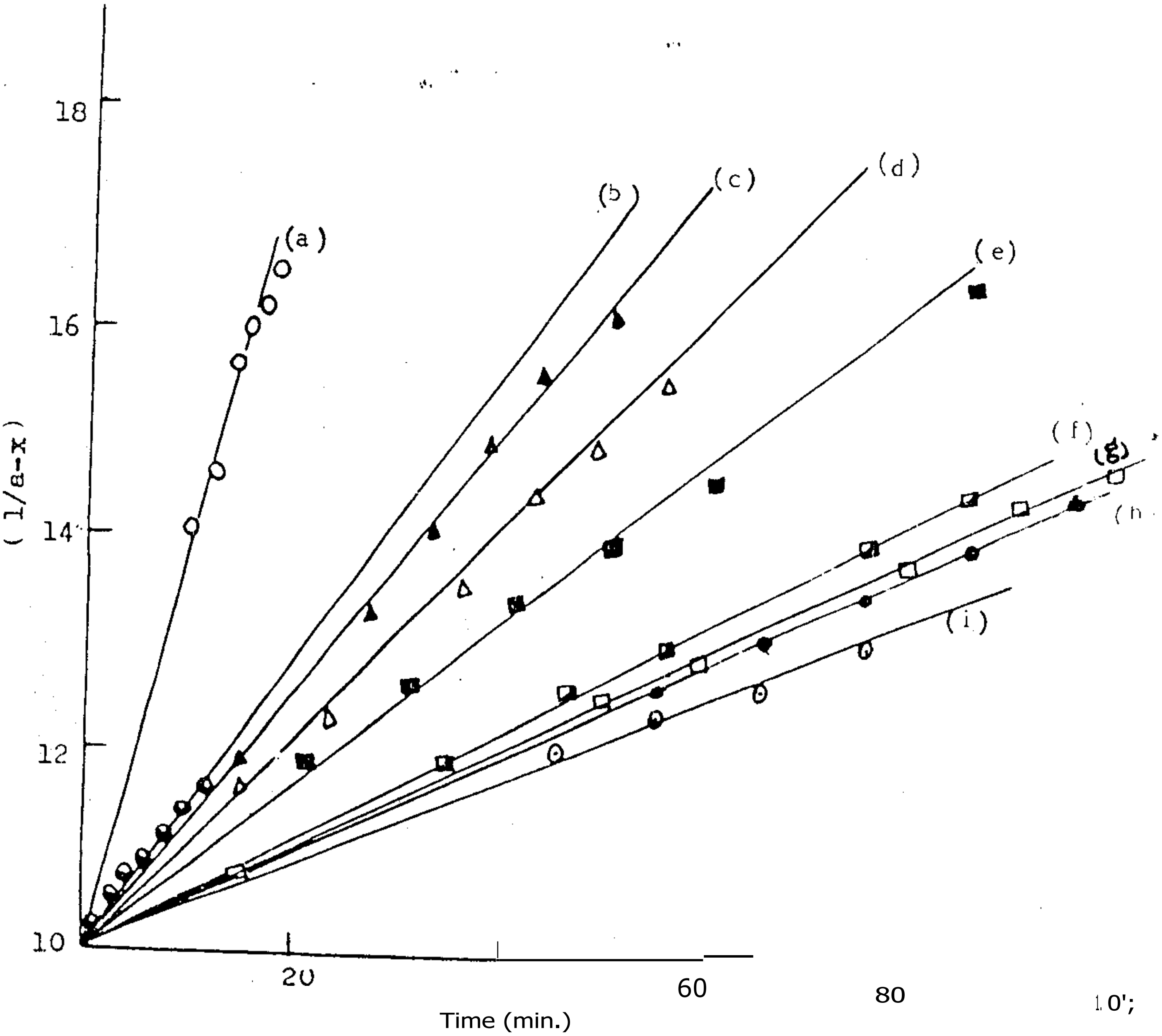

Fig. 4 .Second order rate plots for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane at 50°C in methanol/carbon tetrachloride.

methanol mole fraction

(a) 1.0; (b) 0.8; (c) 0.7; (d) 0.6; (e) 0.5; (f) 0.4; (g) 0.3; (h) 0.2; (i) 0.1•

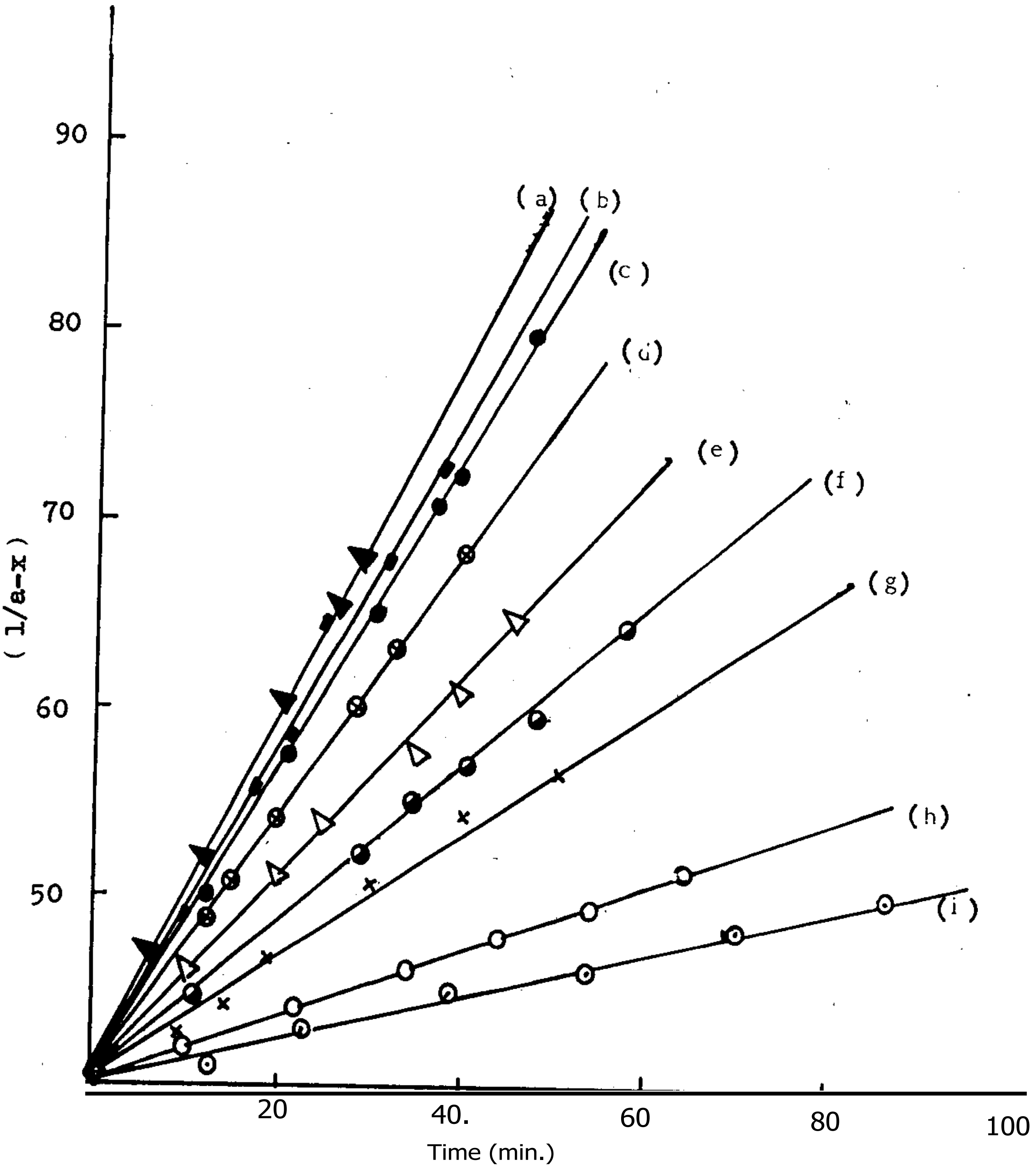

Fig. 5 . Second order rate plots for the dehydripchlorination of ^{1,1} , $^{1-}$trichloro-24-bis-p-chlorophenylethan e at 55°C in methanol /carbon tetrachloride.

methanol mole fraction;

(a) 0.8 ;(b) 0.7i (c) 1.0; (d) (e) 0.5; (f) 0.4; (g) 0.3; (h) 0.2; (i) 0.1

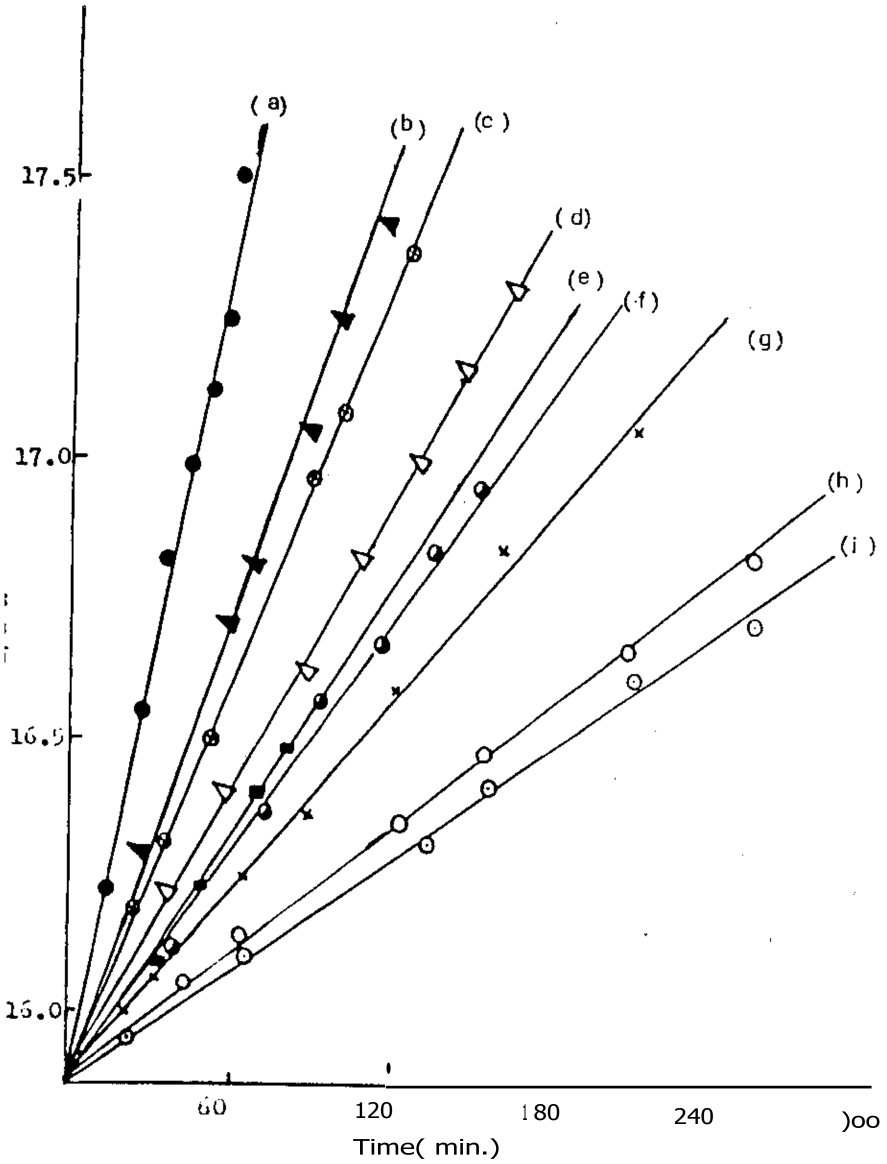

Fig Second order rate ptots for the dehydrouhlorination of 1,1,1-trichloro-2,2-bis-p-methytphenylethane at 53°C in methanol/carbon tetrachloride.

methanol mole fraction:

(a) 0.8 ; (b) 0.7; (c) 0.6; (d) 0.5; (e) 1.0; (f) 0.4; (g) 0.3;

(h) 0.2 ; (i) 0.1

solutions are listed in Table (3-5).

Figures (7-9) show the variation of the specific rate constant (k) of the dehydrochlorination reaction with solvent compositions . Generally , it can be shown that the k - values change in a non-linear manner with the composition of the solvent . in the case of 1,1,1-trichloro-2,2-diphenylethane the rate increase in a regular manner with methanol addition , fig. (7); whereas in 1,1,1-trichloro-2,2-bis-p-chlorophenylethane and 1,1,1-trichloro-2,2-bis-p-methylphenylethane the rate frist increase up to 0.8 methanol mole fraction , then decrease , Fig. (8-9). Similar behaviour for the specific reaction rate constant was previously reported for other systems and in severl binary solvents (25,59). Mclennan et. a1(52) reported that, rate constants for the dehydrochlorination reaction of 1,1,1-trichloro-2,2-diarylethanes by methoxide ion in pure methanol increases with increasing of methoxide ion concentration. These results are in agreement with our results in the dehydrochlorination of 1,1,1-trichloro-2,2-diarylethanes in methanol carbon tetrachloride mixed solvents . The interpretation of solvent effects in terms of degree of solvation of ground and transation states or of specific solvation effects (giving in the present study special priority to methanol as an ion solvator) has been regarded in some cases as an oversimplificiation because more complicated interactions are taking place (19). However in the present study departure from linearity may be attributed to preferential solvation of the activated complex by methanol molecules as will be, justified by the calculated activation parameters.

Table . 3 . Rate constants for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane in methanol / carbon tetrachloride solvent mixtures

Methanol mole fraction	30 °C 0.5°C $K\ x_1 10_1^{-5}$ I mo1 S	35 °C± 0.5°C $K\ x\ 10^{5}_{I}$ 1 moll S	45 °C± 1°C $K\ x\ 10^{5}_{1}$ 1 moll S	50.°C ± 1°C $K\ x\ 10^{5}$ 1 moll S1
0.1	12.50 ±0.12	29.00 ± 0.20	49.50± 0.34	67.40±0.40
0.2	15.60+ 0.10	27.00± 0.24	47.90± 0.22	71.40 ± 0.52
0.3	18.50 ± 0.20	30.00± 0.31	61.60± 0.41	73.50± 0.50
0.4	22.00 ± 0.20	35.40± 0.22	63.30± 0.54	80.50± 0.63
0.5	30.20 ± 0.20	38.20± 0.35	64.10± 0.30	129.00 ± 0.60
0.6	31.20 ± 0.31	53.00± 0.42	79.10± 0.61	171.00± 0.71
0.7	39.50 ± 0.30	62.50± 0.50	100.00± 0.50	216.601 0.76
0.8	45.80 ± 0.42	63.88± 0.44	106.70± 0.64	233.00 ± 0.66
1.0	54.10 ± 0.50	71.75±-0.63	118.00± 0.62	260.00± 0.81

Table . 4 . rate constants fro the dehydrochlorination of 1,1,1-tirchloro-2,2-bis-p-chlorophenylethane in methanol / cxarbon tetrachloride solvent mixtures

Methanol mole fraction	35°C I 0.5°C $K \times 10^{4}$ 1 moi' cl	45°C $^{-1}$ 0.5°C $K \times 10^{4}$ I moll S^{-1}	50°C^{1} 1°C $K \times 10^{4}$ I mol^{l} s^{-l}	55°C± 1°C $K \times 10^{4}$ I mol^{l} s^{-I}
0.1	3.47 ^{1} 0.17	7.18± 0.29	17.78 ^{1} 0.89	20.83 ± 1.25
0.2	5.21 ^{1} 0.21	15.42^{1} 0.85	29.17 ^{1} 1.60	32.81 ± 1.80
0.3	8.89 ^{1} 0.58	18.05± 1.58	40.00 ^{1} 2.40	55.21 ±2.72
0.4	12.10 ^{1} 0.44	29.44^{1} 1.16	53.33 ^{1} 2.66	66.66 ^{1} 4.62
0.5	16.97 ^{1} 0.72	41.66^{1} 1.06	77.77 ^{1} 5.05	88.88 ±2.69
0.6	24.87 ^{1} 1.49	50.00^{1} 1.25	86.00 ^{1} 2.15	111.11 ^{1} 6.90
0.7	43.77 ^{1} 0.66	83.33^{1} 3.93	116.66 ^{1} 8.11	143.94 $^{1-}$10.30
0.8	52.78 ^{1} 1.93	87.30^{1} 2.81	133.3 3^{1} 13.33	155.55 ^{1}11.54
1.0	50.69 ^{1} 2.06	77.08± 2.69	123.30 ^{1} 7.39	138.88 ± 9.00

Table . 5 . Rate constants for the dehydrochlorination of 1,1,1-trichloro-2,2-bis-p-methylphenylethane in methanol / carbon tetrachloride solvent mixtures

Methanol mole fraction	35°C ±0.5°C K x 10^{5} 1 mol^{1} S^{1}	45°C ±0.5°C K x 10^{5} I mol^{l} S^{I}	50°C ± 1°C K x 10^{5} 1 mol^{l} S^{I}	53°C ± 1°C K x 10^{5} 1 mol^{-1} S^{-1}
0.1	2.77 ± 0.05	4.44± 0.13	5.97± 0.23	6.06 ± 0.29
0.2	3.06 ± 0.05	5.92± 0.26	6.25± 0.43	7.08± 0.42
0.3	4.16 ±0.16	7.22± 0.50	8.33± 0.35	nioa± 0.96
0.4	5.55 ±0.17	9.26± 0.32	10.00± 0.70	12.50 ± 0.80
0.5	6.90 ± 0.34	10.37± 0.62	11.61± 0.46	14.16± 0.52
0.6	11.90± 0.24	13.33± 0.53	14.44± 0.62	18.33± 0.49
0.7	17.50± 1.05	20.00± 0.84	22.21± 0.68	25.00± 0.71
0.8	27.75± 1.66	33.33± 0.66	36.00± 0.74	38.33± 0.90
1.0	9.70 ± 0.29	11.11± 0.32	12.50± 0.47	13.33± 0.64

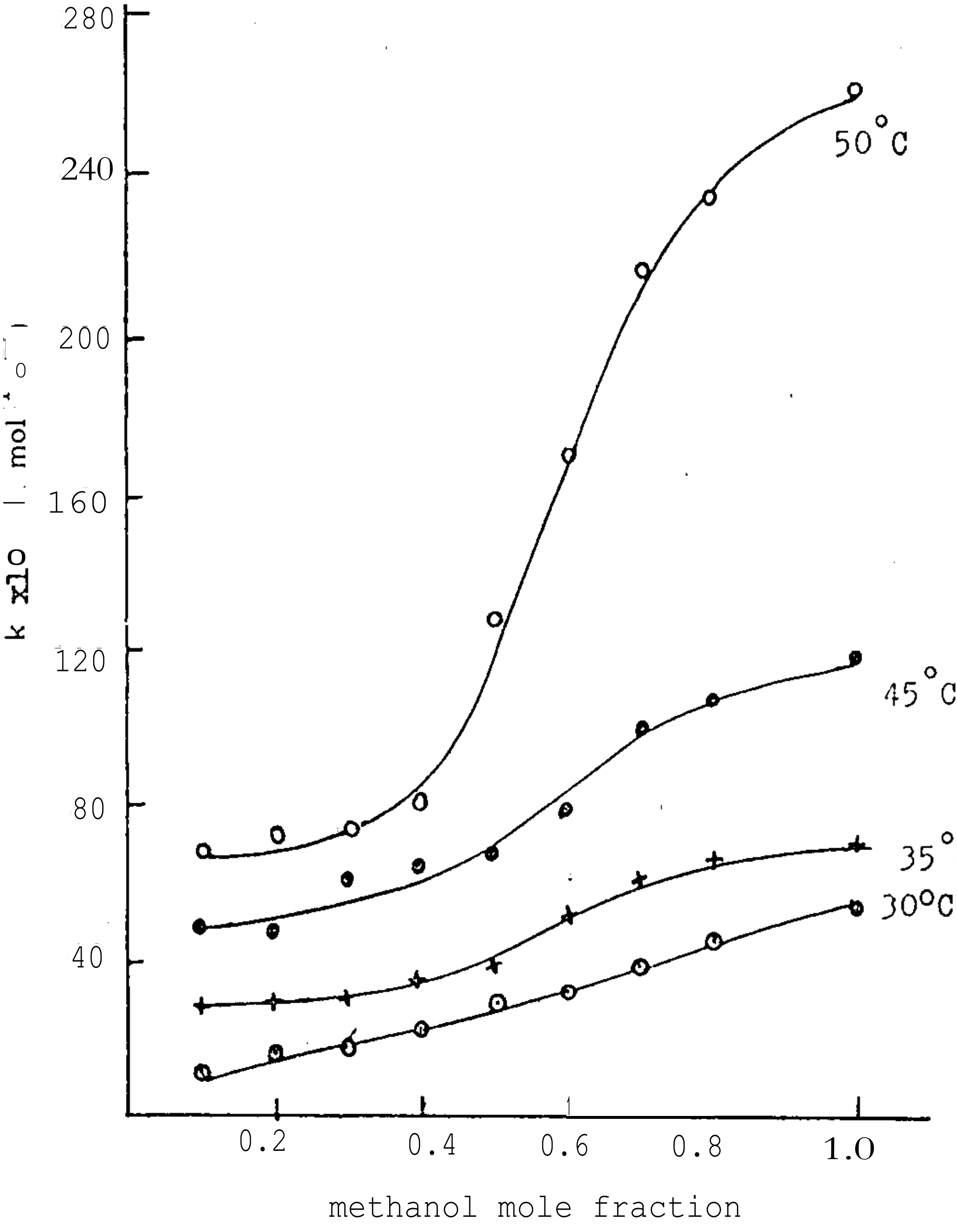

Fig. 7. Dependence of the second order rate constants on solvent composition for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane in methanol-carbon tetrachloride.

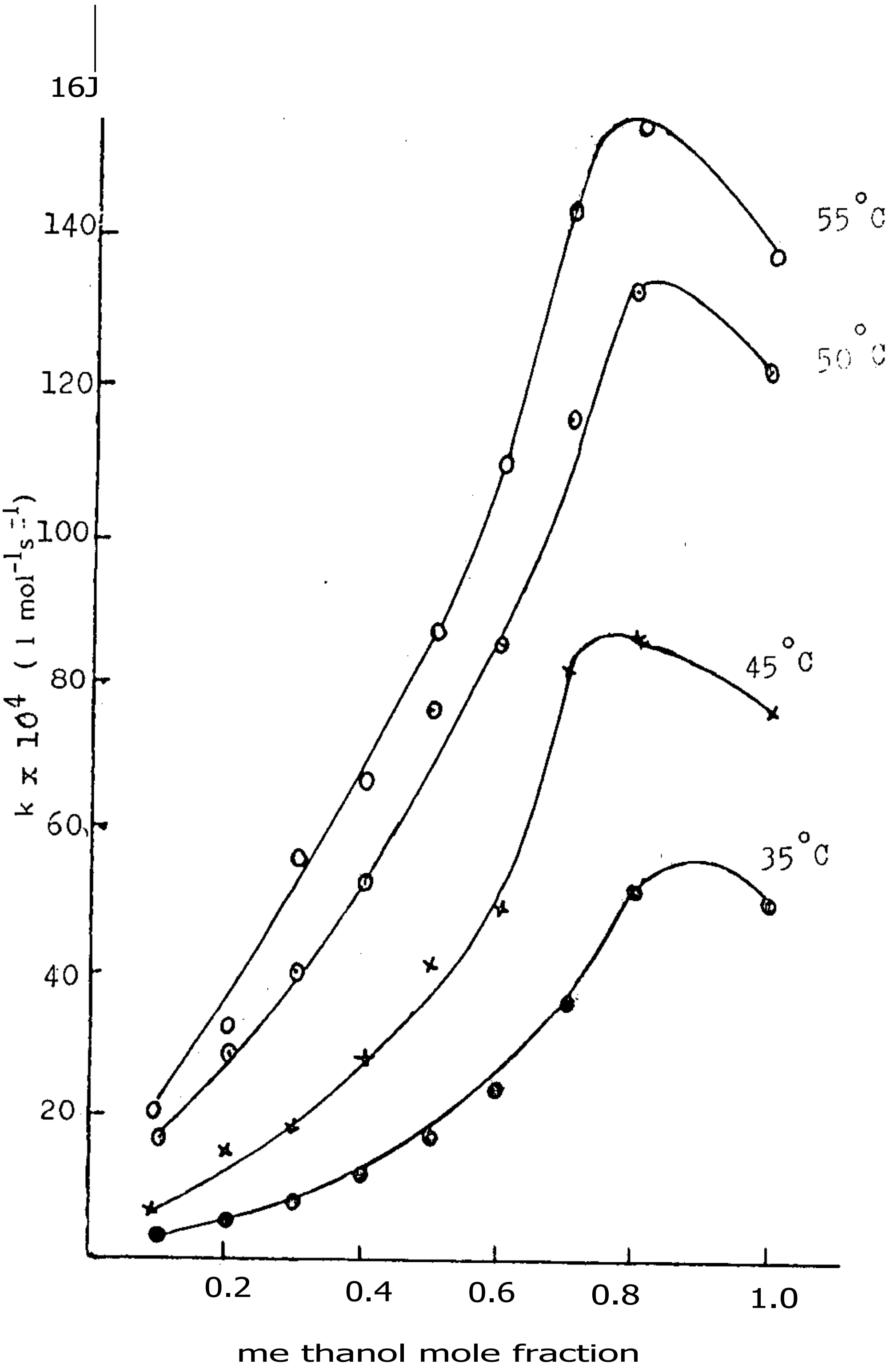

Fig. 8. Dependence of the second order rate constants on solvent composition for the dehydrochlorination of 1,1,1-trichloro-2,2-bis-p-chlorophenylethane in methanol-carbon tetrachloride.

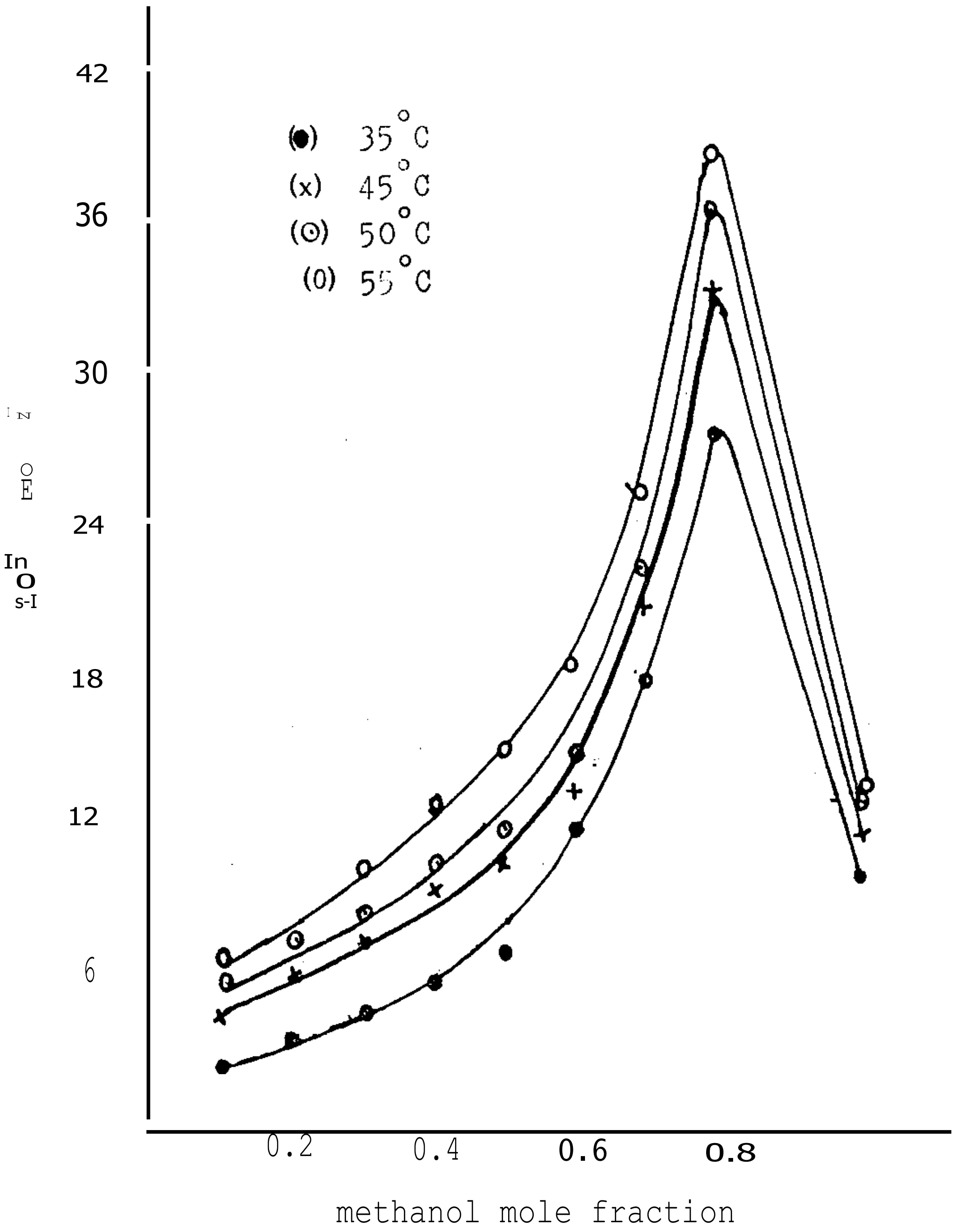

Fig. 9. Dependence of the second order rate constants on solvent composition for the dehydrochlorination of 1,1,1-trichloro2,2-bis-p-methylphenylethane in methanol-carbon tetrachloride.

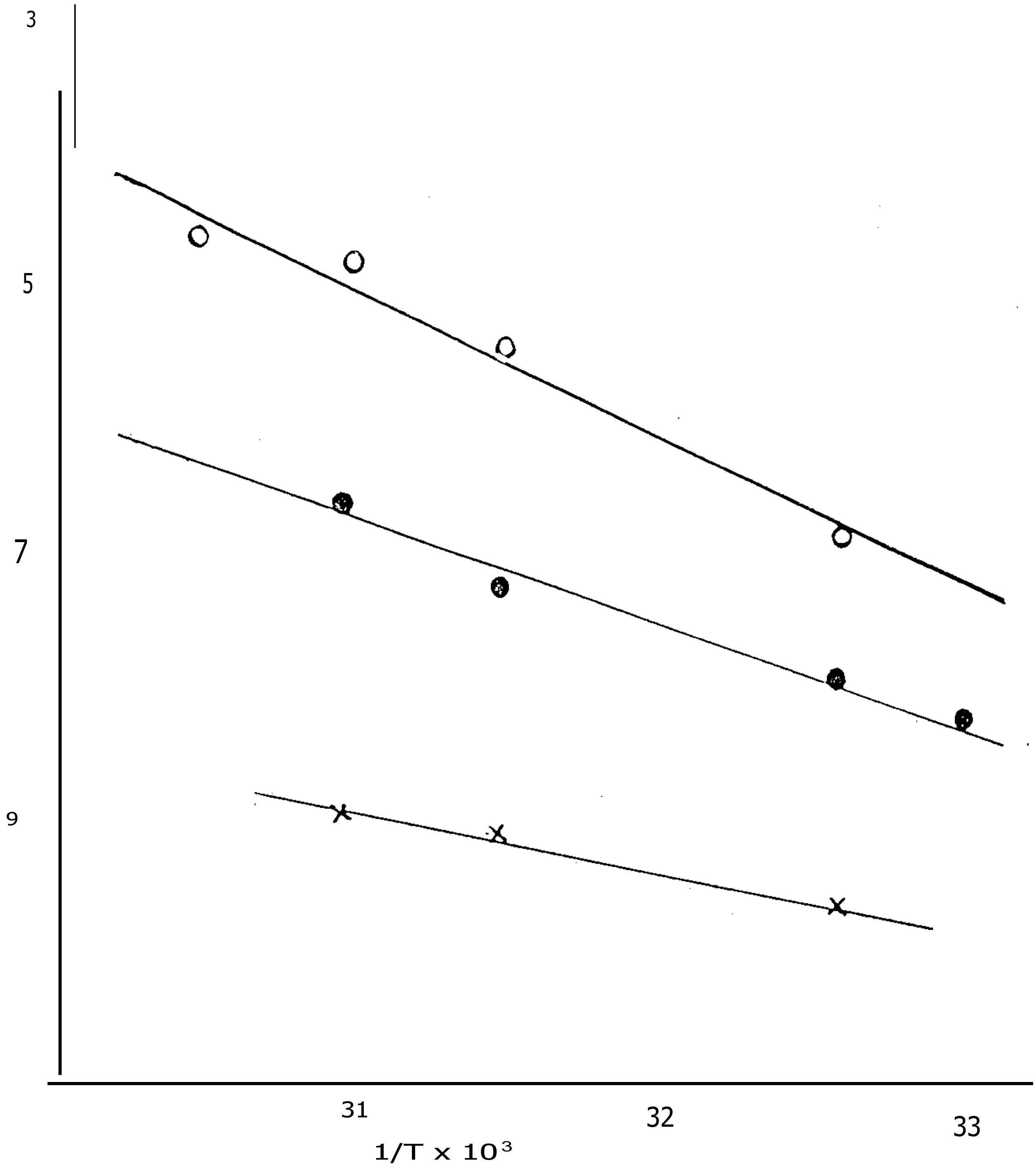

Fig .10. Arrhenius plot of Ink vs. 1/T for (0) 1,1,1-trichloro-2,2-bis-p-chlorophenylethane, (•) 1,1,1-trichloro-2,2-diphenylethane and (X) 1,1,1-trichloro-bis-p-methylphenylethane compounds in methanol/carbontetrachloride solutions.

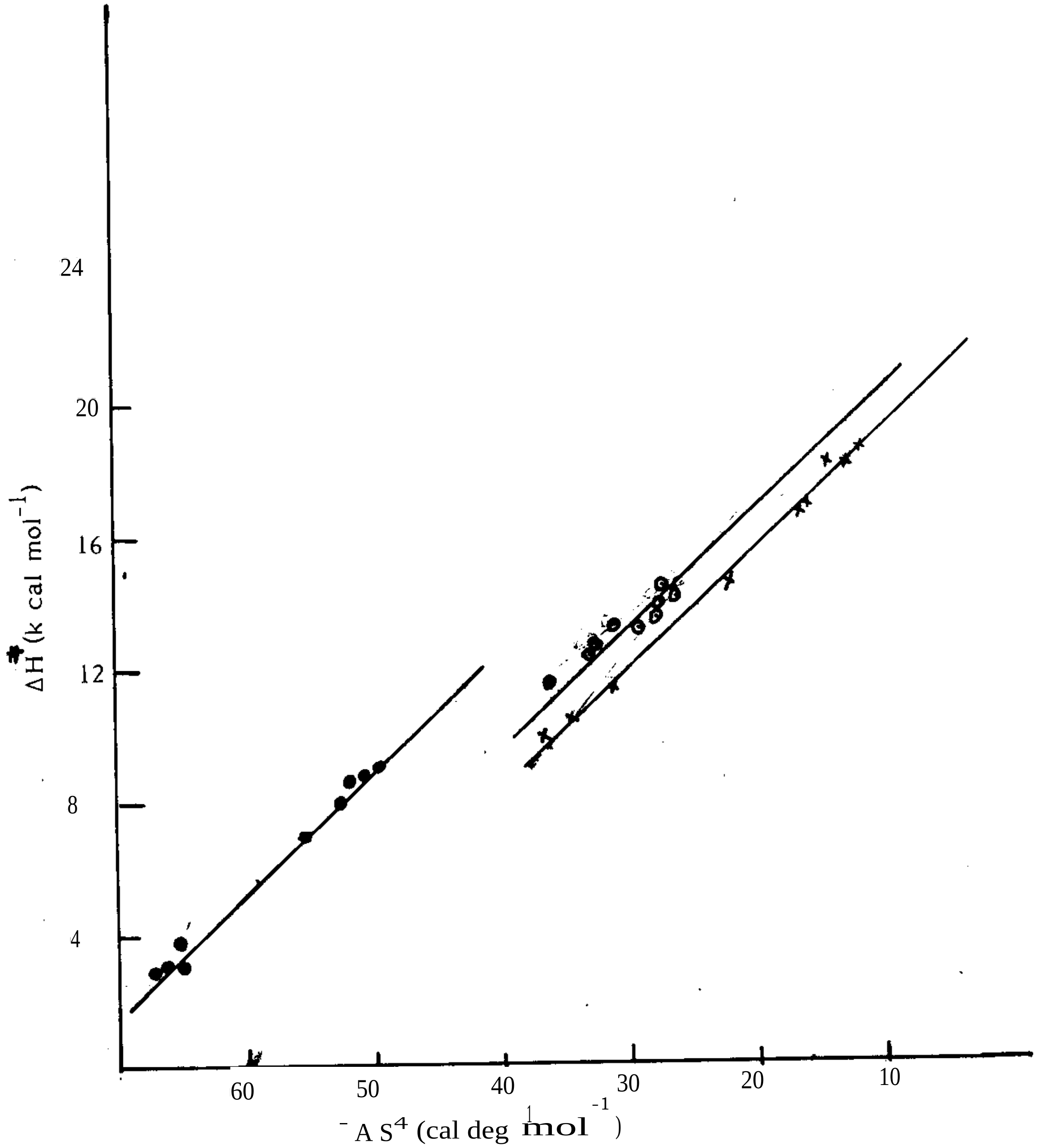

Fig .11. Plots of PH* vs.6,5 for the dehydrochlorination of (0) 1,1,1-trichloro-2,2-diphenylethane, (X) 1,1,1-trichloro-2,2-bis-p-chlorophenylethane and (•) 1,1,1-trichloro-2,2-bis-p-methylphenylethane in methanol-carbon tetrachloride solution.

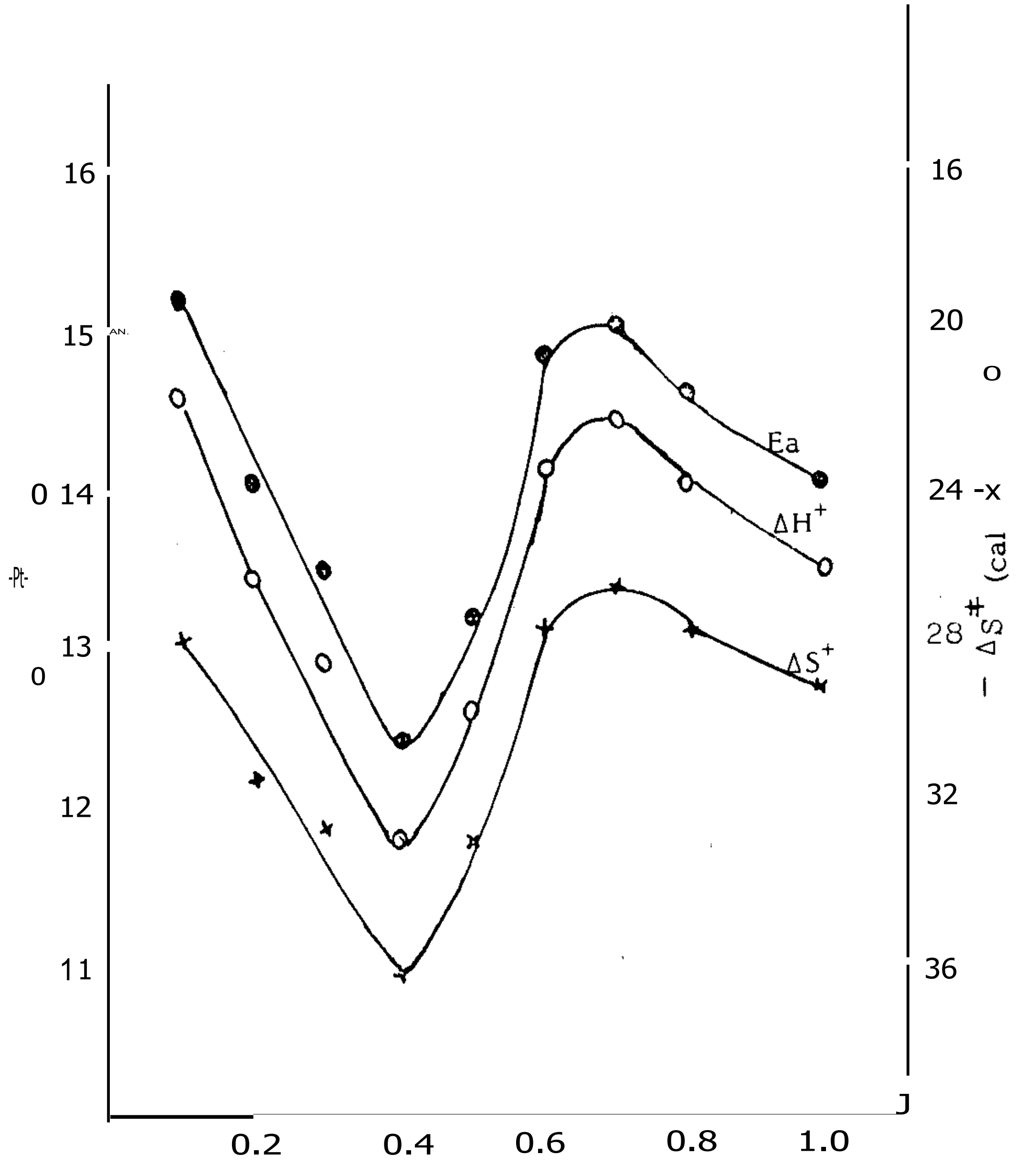

Fig.12. Dependence of the activation parameters Ea,o H^{*}andA S on solvent composition for the clehydrochlorination of 1,1,1-tirchloro-2,2-diphenylethane at 45°C in methanol/carbon tetrachloride.

nol mole fraction. However , the variation of activation parameters with solvent composition for the dehydrochlorination of 1,1,1-trichloro-2,2-bis-p-chlorophenylethane and for 1,1,1-trichloro-2,2-bis-p-methylphenylethane both showed no minima but a maximum at about 0.2 methanol mole fraction as shown in Fig. (13-14), respectively. It can also be seen from the data listed in Table (6) that a large entropy of activation is associated with a large enthalpy of activation and small entropy with a small enthalpy. This is characteristic of reactions involving moderate changes in structure or solvent composition as suggested by Leffler (63).

The free energy of activation , p G , shows , little changes with solvent composition and a plot of A S aganist 4H , Fig. (11), is approximately a straight line. This compensation effect is frequently the case for given reaction investigated in a series of solvents and is possible because there is a general tendency in solution for enthalpy and entropy to compensate each other , so that the net changes in free energy are much smaller (2,64).

3) Solvent Effects on the Rates of dehydrochlorination reaction:-

The dehydrochlorination of 1,1,1-trichloro-2,2-diaryle1hane derivatives by base passes through a transation state in which separation of charge in the organic substrate has taken place. Therefore according to the electrostatic theory an increase in the rate with increasing dielectric constant (D) must be observed and a linear relation between In k and 1/D is to be expected. The dielectric constant values of each solvent mixture were estimated from the dielectric constant values of pure solvents assuming linear dependence on composition. The dielectric constant values of methanol / carbon tetrachloride mixtures at different temperatures are given in Tables (7-9). Figs. (15-17) shows that

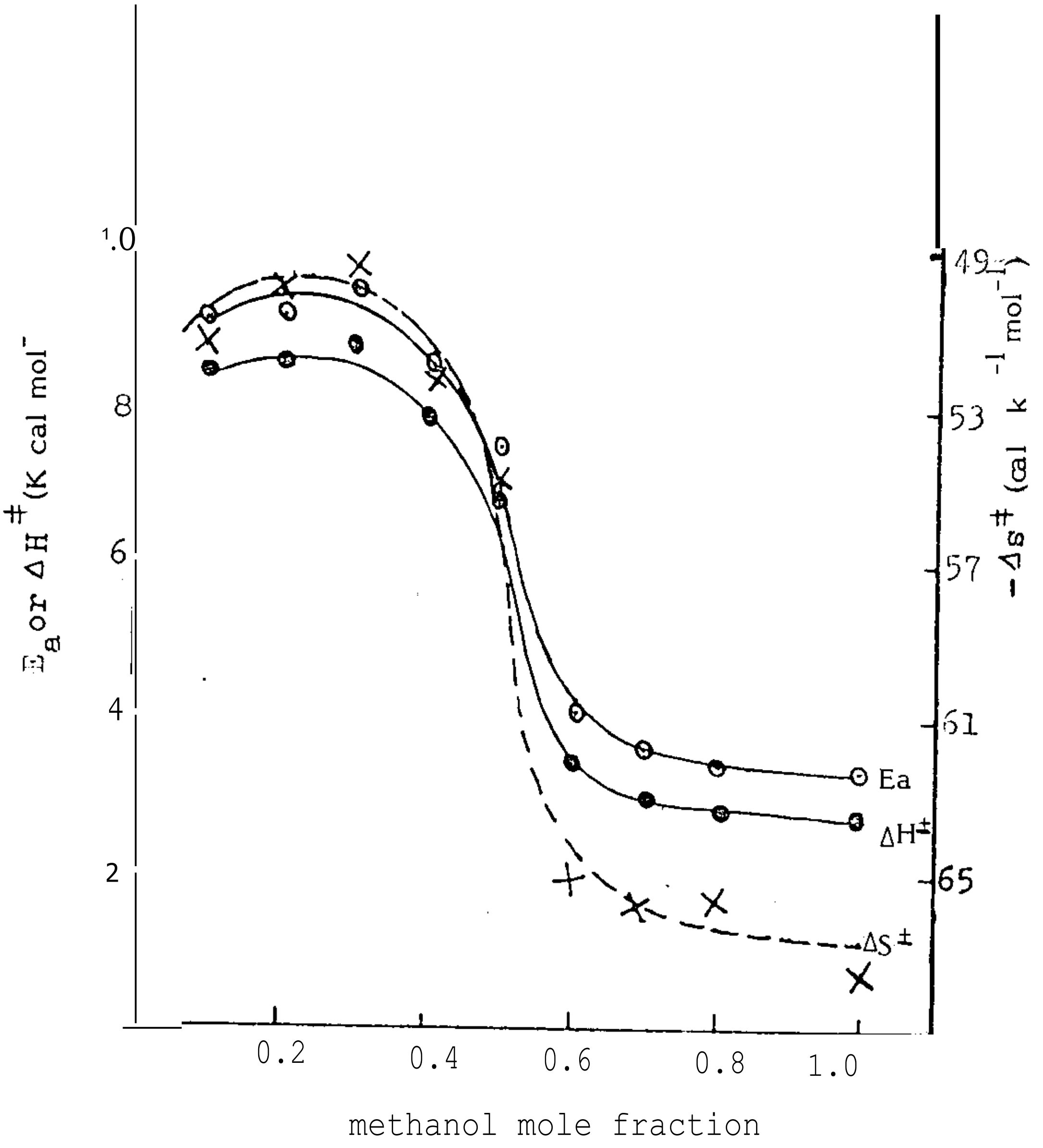

Fig .14. Dependence of the activation parameters Ea,A li*and AS* on solvent composition for the dehydrochlorination of 1,1,1-trichloro-2,2-bis-p-methylphenylethane at 45°C in methanol/carbon tetrachlride.

Table . 7 . dependence of the rate constant for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane in methanol/carbon tetrachloride on dielectric constant of the medium

Methanol mole traction	C°	$K \times 10^5$ 1 ma! $^{-1}$ s^{-1}		$(VD) \times 10^2$
0.1	30	12.50	5.356	18.67
	35	29.00	5.347	18.70
	45	49.50	5.325	18.78
	50	67.40	5.313	18.82
0.2	30	15.60	8.496	11.77
	35	27.00	8.496	11.78
	45	47.90	8.467	11.81
	50	71.40	8.453	11.83
0.3	30	18.50	11.641	8.59
	35	30.00	11.614	8.61
	45	61.60	11.600	8.62
	50	73.50	11.587	8.63
0.4	30	22.00	14.771	6.77
	35	35.40	14.749	6.78
	45	63.30	14.749	6.78
	50	80.50	14.727	6.79
0.5	30	30.20	17.921	5.58
	35	38.20	17.889	5.59
	45	64.16	17.857	5.60
	50	129.00	17.889	5.59
0.6	30	31.20	21.052	4.75
	35	53.00	21.008	4.76
	45	79.10	21.008	4.76
	50	171.00	22.320	4.48
0.7	30	39.50	24.154	4.14
	35	62.50	24.154	4.14
	45	100.00	24.154	4.14
	50	216.60	24.154	4.14
0.8	30	45.80	27.100	3.69
	35	63.88	27.322	3.66
	45	106.70	27.322	3.66
	50	233.00	27.322	3.66
1.0	30	54.10	33.670	2.97
	35	71.75	33.557	2.98
	45	118.00	33.557	2.98
	50	260.00	33.557	2.98

Table . 8 . dependence of rate constant for the dehydrochlorination of $^{1},^{1},^{1-}$trichlora-2,2-bis-p-chlorophenylethane in methanol/carbon tetrachloride on dielectric constant of the medium.

Methanol mole fraction	°	K x 10^{4} l mol^{-1} S^{-1}		(1/D) x 10^{2}
0.1	35	3.472	5.244	19.068
	45	7.176	5.220	19.156
	50	17.777	5.209	19.197
	55	20.833	5.197	19.192
0.2	35	5.208	8.280	12.076
	45	15.417	8.252	12.118
	50	29.166	8.240	12.135
	55	32.812	8.226	12.156
0.3	35	8.888	11.316	8.836
	45	18.055	11.284	8.861
	50	40.000	11.271	8.871
	55	55.208	11.255	8.884
0.4	35	12.100	14.352	6.967
	45	29.444	14.316	6.984
	50	53.333	14.302	6.991
	55	66.666	14.284	7.000
0.5	35	16.966	17.389	5.751
	45	41.666	17.349	5.764
	50	77.777	17.334	5.769
	55	88.888	17.314	5.775
0.6	35	24.872	20.425	4.895
	45	50.000	20.381	4.906
	50	86.000	20.365	4.910
	55	111.111	20.343	4.915
0.7	35	43.775	23.461	4.262
	45	83.333	24.154	4.140
	50	116.666	23.396	4.274
	55	143.939	23.372	4.274
	35	52.777	26.497	3.773
	45	87.300	26.445	3.781
	50	133.333	26.427	3.783
	55	155.555	26.401	3.787
	35	50.694	32.570	3.070
	45	77.083	32.510	3.075
	50	123.300	32.490	3.077
	55	138.888	32.460	3.080

Table . 9 . dependence of the rate constants for the dehydrochlorination of 1,1,1-trichloro-bis-p-methylphenylethane in methanol/carbon tetrachloride on dielectric constant of the medium.

Methanol mole fraction	C°	K x 10^5 $l\ mol^{-1}\ s^{-1}$	D	(VD) x 10^2
0.1	35	2.77	5.244	19.068
	45	4.44	5.220	19.156
	50	5.97	5.209	19.196
	53	6.06	5.308	18.838
0.2	35	3.06	8.280	12.076
	45	5.92	8.252	12.117
	50	6.25	8.240	12.117
	53	7.08	8.444	11.842
0.3	35	4.16	11.316	8.836
	45	7.22	11.284	8.861
	50	8.33	11.271	8.871
	53	10.00	11.580	8.635
0.4	35	5.55	14.352	6.967
	45	9.20	14.316	6.984
	50	10.00	14.302	6.991
	53	12.50	14.716	6.794
0.5	35	6.913	17.389	5.750
	45	10.37	17.349	5.764
	50	11.61	17.334	5.769
	53	14.16	17.853	5.601
0.6	35	11.90	20.425	4.895
	45	13.33	20.381	4.906
	50	14.44	20.365	4.910
	53	18.33	20.989	4.764
0.7	35	17.50	23.461	4.262
	45	20.00	24.154	4.140
	50	22.21	23.396	4.274
	53	25.00	24.125	4.145
0.8	35	27.75	26.497	3.774
	45	33.33	26.445	3.781
	50	36.00	26.427	3.783
	53	38.33	27.261	3.668
1.0	35	9.70	32.570	3.070
	45	11.11	32.510	3.075
	50	12.50	32.490	3.077
	53	13.33	33.534	2.982

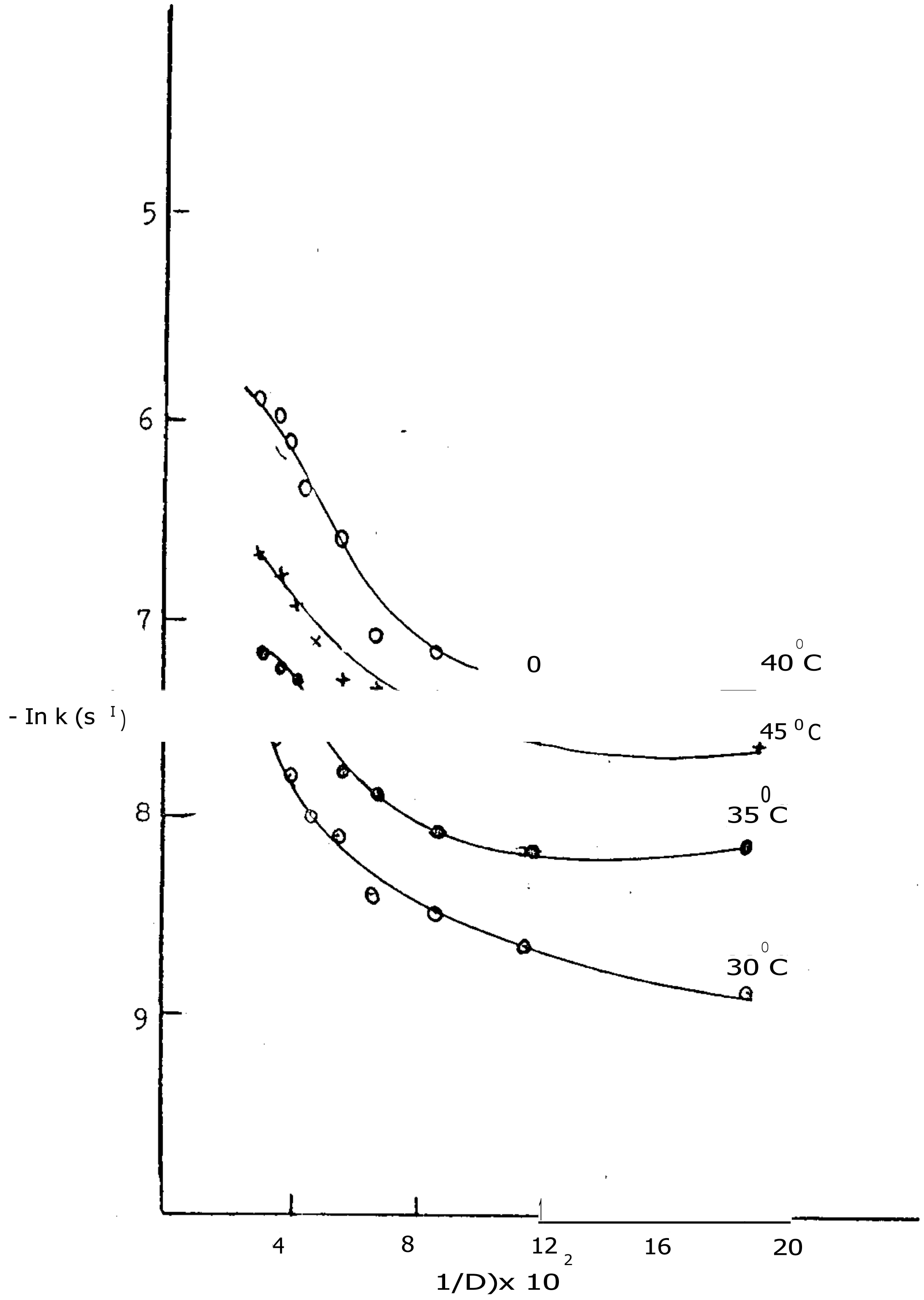

Fig.15 Dependence of the second order rate constants for the dehydrochlorination of 1,1,1-trichloro-2,2-(liphenylethane on the dielectric constant of the medium.

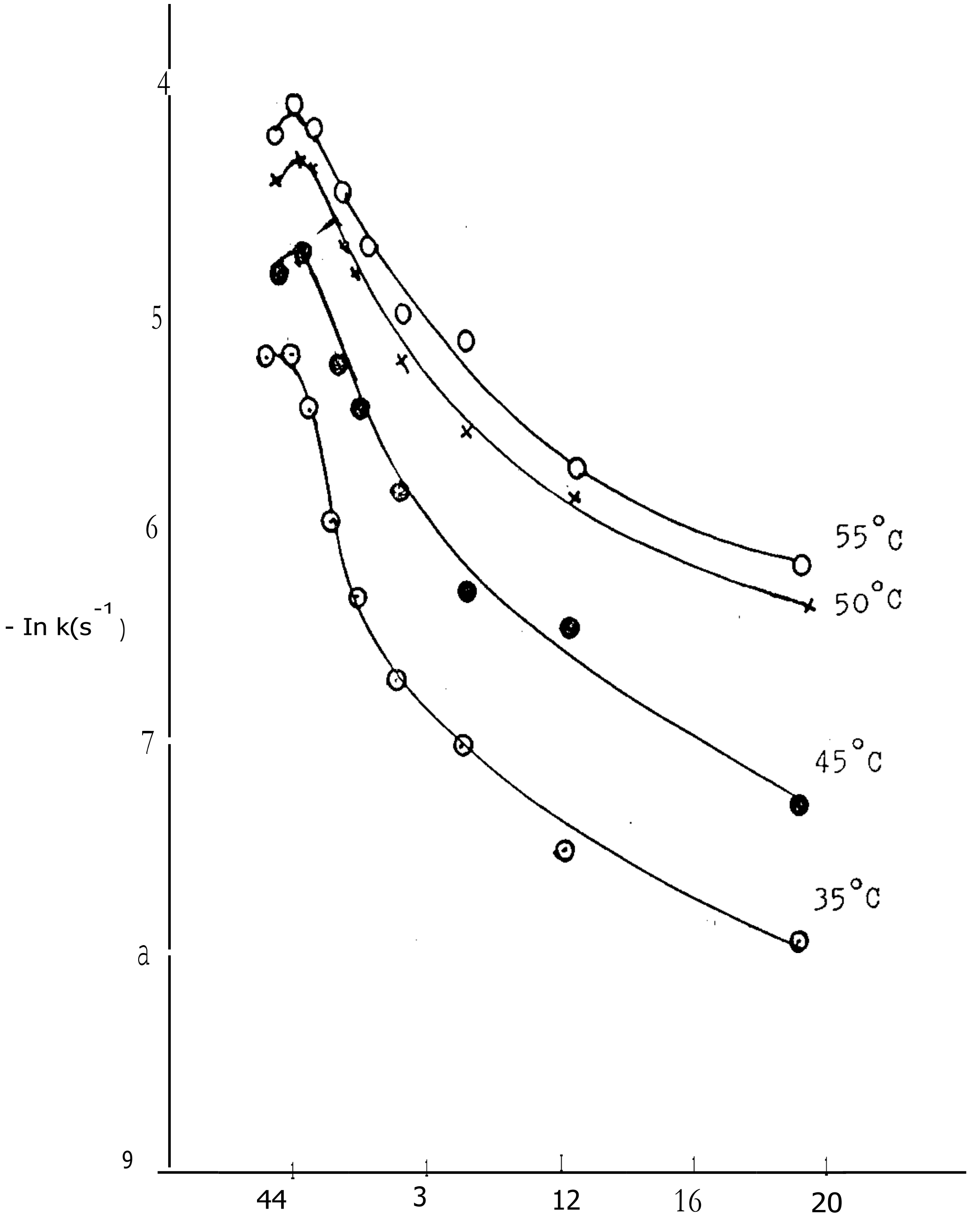

Fig.16. Dependence of second order rate constant for the dehydrochlorination of 1,1,1-trichloro-2,2-b s-p-chlorophenylethane on the dielectric constant of the medium.

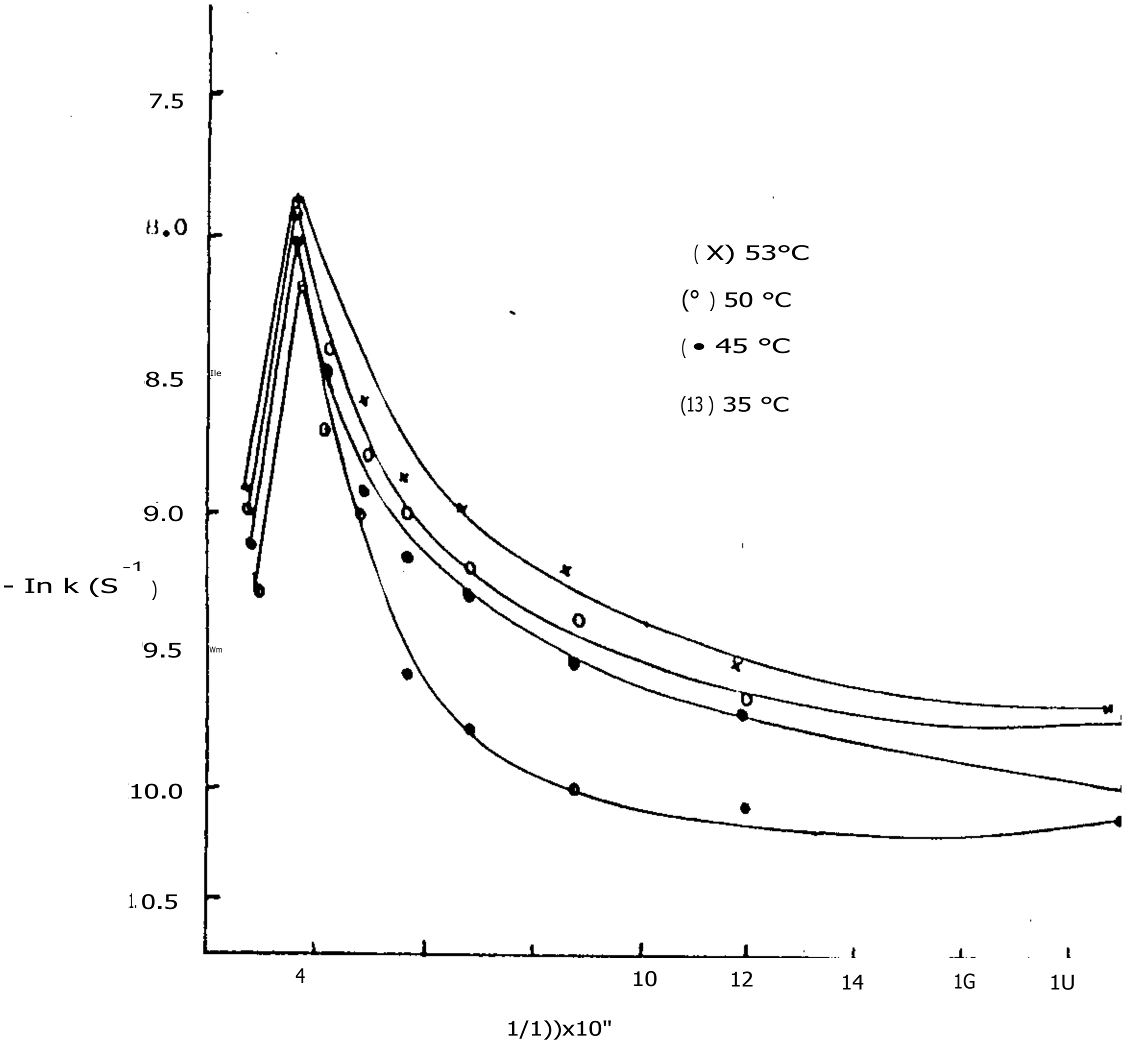

Fig.1 7. Dependence of the second order rate constants for the dehydrochforination of 1,1,1-trichlono-2,2-bis-p-methyl-phenyletha,ne on dielectric costant of the medidm.