estimated by graphical interpolation of his results.

The dielectric constant data for formic acid solutions,[52] piperidine,[53] pyridine,[54] and water[55] were obtained either directly from the literature, interpolated from reported values, or estimated by graphical interpolation.

Plots of the various log k's versus 1/D and versus mole fraction of water, N_{H_2O}, illustrate that only the k_2 values have a linear relationship (see figures 10, 11, 12 and 13). The k_s values for the same coordinates show a non-linear relationship (see figures 11 and 13).

TABLE IV

PHYSICAL CONSTANTS DATA

Sample of Methanol	Approximate M.p., °C.	B.p. °C./mm.Hg	$n_D^{27°}$	$d_4^{25°}$	% H_2O	pH reading
I	-98	64.5/760	1.3310	.7922	.005	7.1
II	-97.8	64.5/760	1.3311	.7922	.004	7.1
III	-97.8	64.5/760	1.3310	.7922	.005	7.1

*Beckmann pH meter reading at 25°C., buffer standardization reading at 25°C. 8.7.

Water   Specific conductivity**   1.2 x 10^{-6} ohm^{-1} cm^{-1}

     $pH_{25}°C.$ 6.92

     n_D^{25} 1.3330

**In air.

TABLE V

PHYSICAL CONSTANTS DATA

n-Butyl bromide:

Approximate, M. p., °C.	-112.5
B_t p., °C. /mm. Hg	101.5/760
n_D^t	1.4360
t °C.	27
d_4^{27}	1.2685
Mr_D calculated:	28.437[a]
observed:	28.222[b]

Methanol-water mixtures:

Weight per cent MeOH	75; 50; 25
n_D^t	1.3381; 1.3411; 1.3381
t °C.	26.5; 26.5; 26.0

[a] Estimated from atomic refractions; [b] calculated from the Lorenz and Lorentz equation.

TABLE VI

A BRIEF SUMMARY OF REACTION PRODUCT ANALYSIS

Solvent	time (approx.)	Temp. °C.	total vol. of mixture	$(BuBr)_0$	$(NaOH)_0$	BuOH, g.	$BuOCH_3$, g.
50 wt.% MeOH-H_2O	8 days	65-70° (reflux)	650 ml.	95.9 g. 1.07M	85 g. 3.26N	28.1 g.	61.78 g.
60 wt.% MeOH-40% H_2O	2 days	30°	500 ml.	13.7 g. 0.2 M	4.03 g. 0.2 N	1.4 g.	3.59g.
90 wt.% MeOH-10% H_2O	13 days	30°	250 ml.	13.7 g. 0.4 M	4.02 g. 0.4 N	.099 g. (trace)	1.7 g.

TABLE VII

Kinetics of the Solvolysis of n-Butyl Bromide
at 50° C. in 50 Weight % Aqueous Methanol and
in the Presence of 0.1 N Sodium Hydroxide*

$t_{min.}$	HC1[a] ml.	$AgNO_3$[b] ml.	(NaOH)[c] mole/l.	(Br⁻) mole/l.	(BuBr)[d] mole/l.
		Run 2			
0	44.80	0.0	.1382	.0000	.1092
61	38.20	5.01	.1178	.0204	.0888
94	35.90	6.74	.1107	.0275	.0817
112	34.39	7.87	.1061	.0321	.0771
124	33.50	8.57	.1033	.0349	.0743
153	33.37	8.69	.1028	.0354	.0738
166	33.58	8.50	.1036	.0346	.0746
171	32.20	9.55	.0993	.0389	.0703
197	31.66	9.95	.0977	.0405	.0687
"∞"	2.30	11.50**	.0071	.1171	-

[a] 0.0617 N; titer, 20 ml. of reaction mixture.

[b] 0.1018 N; titer, 25 ml. of reaction mixture.

[c] $(a-x)_t$, initially a is 0.1382 N.

[d] $(b-x)_t$, initially b is 0.1092 N.

* Methanol I; temperature, 50° ± .05.

** Titer, 10 ml. of reaction mixture.

TABLE VIII

Kinetics of the Solvolysis of <u>n</u>-Butyl Bromide
at 50° C. in 50 Weight % Aqueous Methanol and
in the Presence of o.1 N Sodium Hydroxide

$t_{min.}$	HCl[a] ml.	AgNO$_3$[b] ml.	(NaOH)[c] mole/l.	(Br⁻) mole/l.	(BuBr)[d] mole/l.
			Run 3		
0	21.55	0.0	.1330	.0000	.1104
57	19.35	1.86	.1194	.0189	.0915
251	14.01	4.99	.0865	.0508	.0596
311	13.07	5.70	.0807	.0580	.0524
335	12.46	5.95	.0769	.0606	.0498
366	11.60	6.18	.0716	.0629	.0475
388	11.28	6.35	.0696	.0646	.0458
412	11.00	6.36	.0672	.0648	.0456
444	10.53	6.40	.0650	.0651	.0453
470	10.20	6.75	.0629	.0687	.0417
481	10.17	6.90	.0625	.0702	.0402
582	9.20		.0568		
583		7.45		.0758	.0346
633	8.80		.0543		
634		7.48		.0761	.0343
676	8.43		.0520		
678		7.75		.0789	.0315
1440	7.30	8.72	.0448	.0888	.0216
1473		8.78		.0894	.0210
"∞"	0.02	10.84	.0001	.1103	.0001

[a] 0.0617 N; [b] 0.1018 N; [c] (a-x)$_t$ initially, a is
0.1330 N; [d] (b-x)$_t$, initially b is 0.1104 M.

Methanol I; temperature, 50° ± .05; titer, 10 ml.
of reaction mixture in all cases.

TABLE IX

Kinetics of the Solvolysis of <u>n</u>-Butyl Bromide
at 50° C. in 75 Weight % Aqueous Methanol and
in the Presence of 0.1 N Sodium Hydroxide*

$t_{min.}$	HCl[a] ml.	$AgNO_3$[b] ml.	(NaOH)[c] mole/l.	(Br⁻) mole/l.	(BuBr)[d] mole/l.
			Run 4		
0	24.70	0.0	.1534	.0000	.1110
42	23.53	1.45	.1452	.0148	.0962
58	23.03	1.82	.1421	.0185	.0925
74	22.28	2.18	.1375	.0222	.0888
88	21.62	2.37	.1334	.0241	.0869
177	19.23	3.57	.1187	.0363	.0747
195	18.75	3.81	.1157	.0388	.0722
238	18.23	4.40	.1125	.0448	.0662
252	18.05	4.46	.1114	.0454	.0656
363	15.78	5.20	.0974	.0529	.0581
374	15.65	5.34	.0960	.0544	.0566
437	14.71	6.20	.0908	.0631	.0479
475	14.15	6.28	.0877	.0640	.0470
492	13.92	6.38	.0859	.0649	.0461
536	13.20	6.69	.0814	.0682	.0428
552	13.14	6.75	.0811	.0694	.0416
599	13.03	7.02	.0804	.0715	.0395
618	12.96	7.10	.0800	.0723	.0387
658	12.82	7.21	.0791	.0734	.0376
672	12.72	7.25	.0785	.0738	.0372
741	12.25	7.28	.0756	.0741	.0369
753		6.10**		.0776	.0334
	-----	10.90	-----	.1110	-----

[a] 0.0617 N; [b] 0.1018 N; [c] $(a-x)_t$, initially a is
0.1534 N; [d] $(b-x)_t$, initially b is 0.1110 M; *temp-
erature, 50° ± .05; methanol II; titer, 10 ml. of
reaction mixture in all but one case; ** titer, 8 ml.
of reaction mixture.

TABLE X

Kinetics of the Solvolysis of n-Butyl Bromide at 50° C. in 75 Weight % Aqueous Methanol and in the Presence of 0.1 N Sodium Hydroxide*

$t_{min.}$	HCl[a] ml.	AgNO$_3$[b] ml.	(NaOH)[c] mole/l.	(Br$^-$) mole/l.	(BuBr)[d] mole/l.
		Run 7			
0	24.79	0.0	.1530	.0000	.1109
30	23.93		.1477		
140	20.20	3.08	.1246	.0314	.0795
220	18.46	4.21	.1139	.0429	.0680
309	17.01	4.83	.1050	.0492	.0617
412	15.05	5.84	.0929	.0595	.0514
579	13.09	6.92	.0808	.0705	.0404
703	11.66	7.25	.0720	.0739	.0370
790	10.74	7.84	.0663	.0799	.0310
870	10.21	8.24	.0630	.0839	.0270
"∞"	-----	10.90	-----	.1110	-----

[a] 0.0617 N; titer, 10 ml. of reaction mixture.

[b] 0.1018 N; titer, 10 ml. of reaction mixture.

[c] $(a-x)_t$, initially a is 0.1530 N.

[d] $(b-x)_t$, initially b is 0.1109 M.

* Methanol II; temperature, 50° ± .05.

TABLE XI

Kinetics of the Solvolysis of n-Butyl Bromide
at 50° C. in 25 Weight % Aqueous Methanol and
in the Presence of 0.1 N Sodium Hydroxide*

$t_{min.}$	HCl^a ml.	$AgNO_3^b$ ml.	$(NaOH)^c$ mole/l.	(Br^-) mole/l.	$(BuBr)^d$ mole/l.
			Run 5		
0	11.70	0.0	.0722	.0000	.0696
72		0.720		.0073	.0623
73	11.05		.0682		
153	10.55		.0651		
154		0.925		.0094	.0602
206		1.098		.0112	.0584
208	10.28		.0634		
272	9.87	1.238	.0609	.0126	.0570
328	9.70	1.378	.0598	.0140	.0556
414	9.30	1.580	.0574	.0161	.0535
450	9.15	1.645	.0564	.0167	.0529
511	8.75	1.795	.0540	.0183	.0513
836	7.88	2.467	.0486	.0251	.0445
889	7.70	2.540	.0475	.0258	.0438
1055	7.00	2.850	.0432	.0290	.0406

[a] 0.0617 N; titer, 10 ml. reaction mixture.

[b] 0.1018 N; titer, 10 ml. reaction mixture.

[c] $(a-x)_t$, initially a is 0.0722 N.

[d] $(b-x)_t$, initially b is 0.0696 M.

* Methanol III; temperature, 50° ± .05; note that the concentrations of a and b are smaller than those in runs for other solvent mixtures.

TABLE XII

Kinetics of the Solvolysis of <u>n</u>-Butyl Bromide
at 50° C. in 25 Weight % Aqueous Methanol and
in the Presence of 0.1 N Sodium Hydroxide*

$t_{min.}$	HCl^a ml.	$AgNO_3^b$ ml.	$(NaOH)^c$ mole/l.	(Br^-) mole/l.	$(BuBr)^d$ mole/l.
		Run 6			
0	11.54	0.0	.0712	.0000	.0643
112	10.81	0.42	.0667	.0043	.0600
370	9.97	1.031	.0615	.0105	.0538
582	9.24	1.414	.0570	.0144	.0499
670	8.75	1.67	.0541	.0171	.0472
735	8.61	1.797	.0531	.0183	.0460
790	8.49	1.87	.0524	.0190	.0453
1022	7.79	2.337	.0481	.0238	.0405
1125	7.50	2.475	.0463	.0252	.0391

[a] 0.0617 N; titer, 10 ml. reaction mixture.

[b] 0.1018 N; titer, 10 ml. reaction mixture.

[c] $(a-x)_t$, initially a is 0.0712 N.

[d] $(b-x)_t$, initially b is 0.0643 M.

* Methanol III; temperature, 50° ± .05; note that the concentrations of a and b are smaller than those in runs for other solvent mixtures.
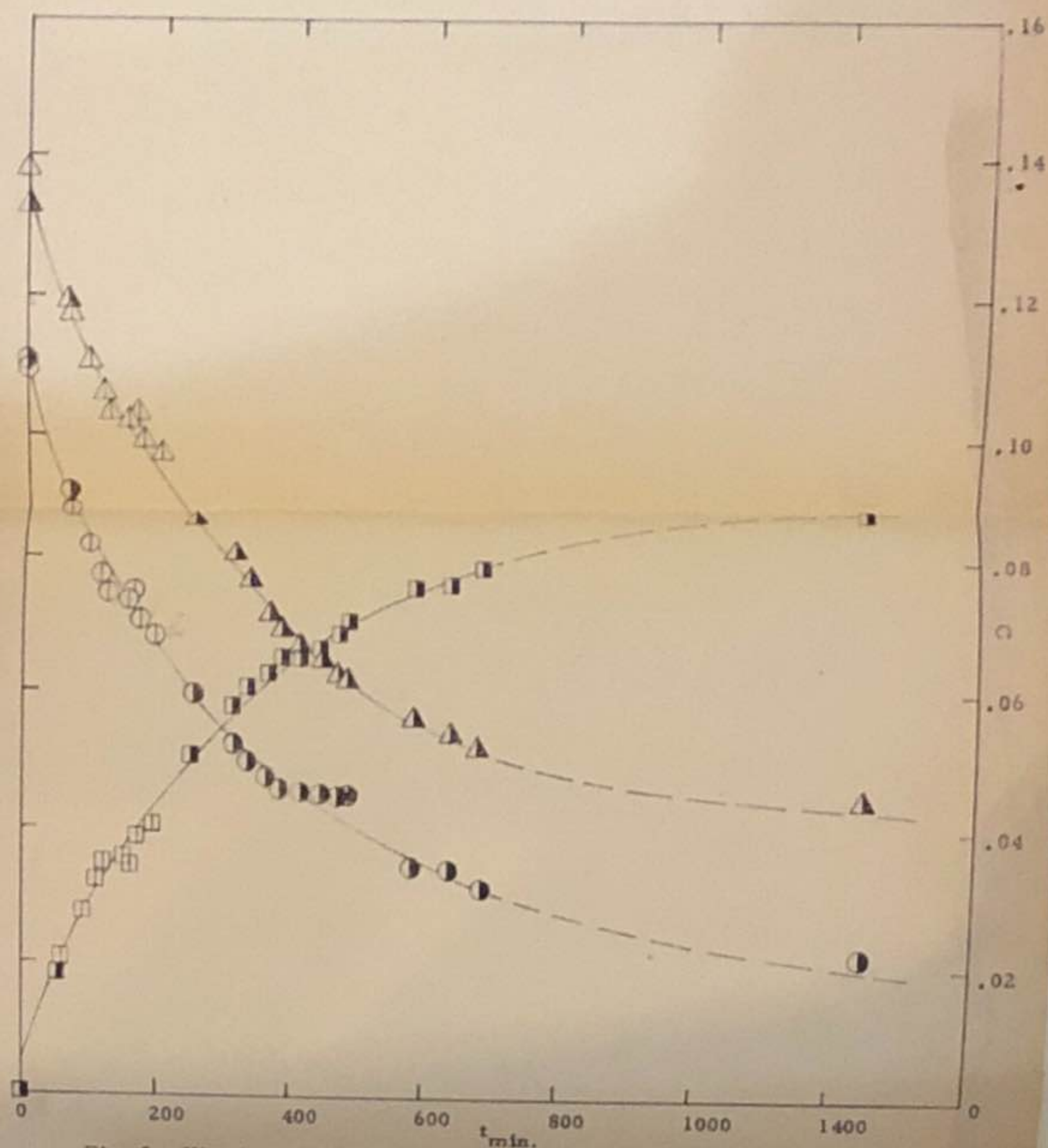
Fig. 5. Kinetics of the Solvolysis of n-Butyl bromide in the presence of Sodium hydroxide in 50% Methanol-50% Water (by weight) at 50° C. (Br⁻): ◼, run 3; ◫, run 2. (BuBr): ◖, run 3; ◒, run 2. (OH⁻): ▲, run 3; △, run 2.
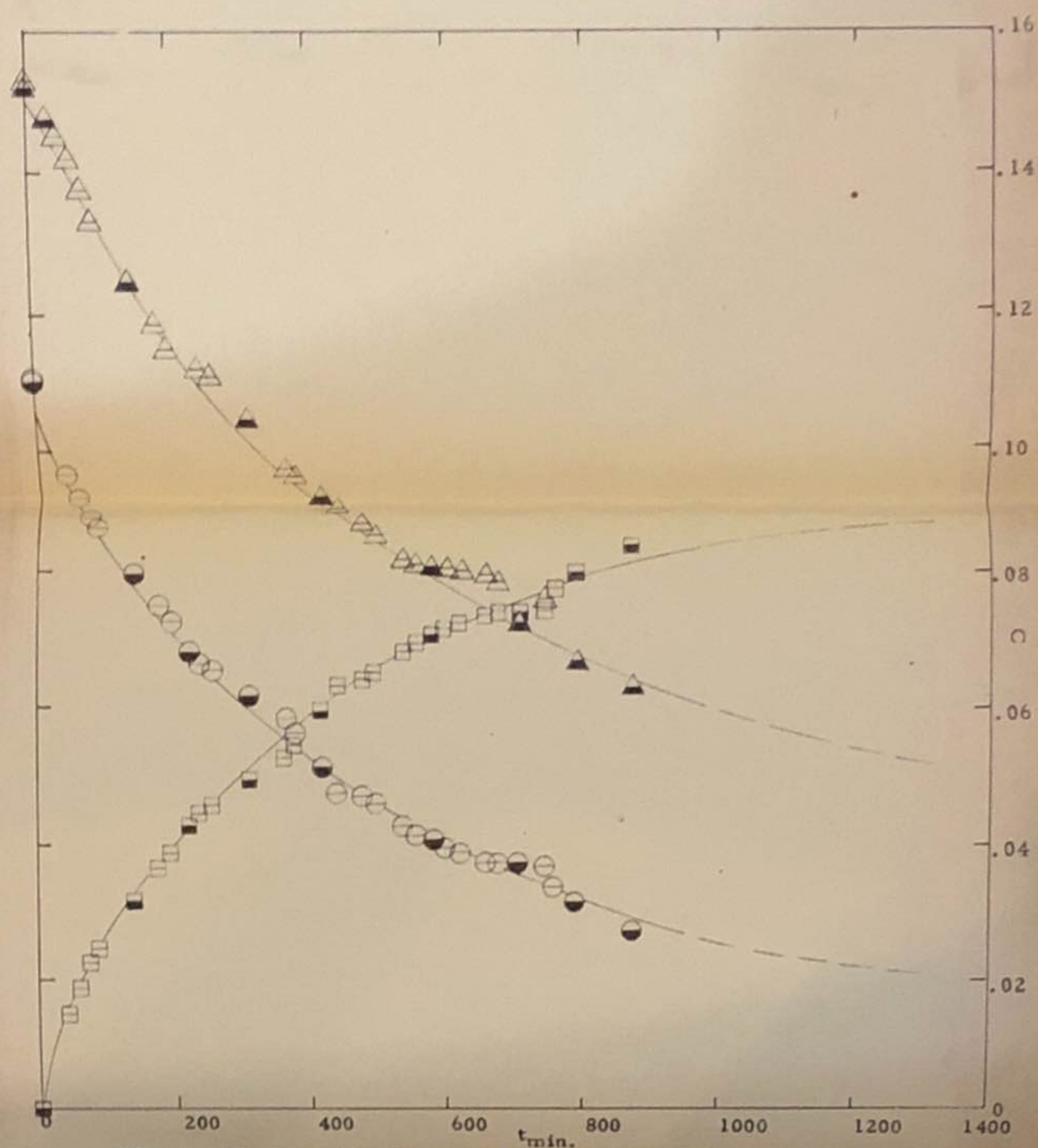
Fig. 6. Kinetics of the Solvolysis of n-Butyl bromide in the presence of Sodium hydroxide in 75% Methanol-25% Water (by weight) at 50° C. (Br^-): ▣ , run 7; ⊟ , run 4. (BuBr): ◐ , run 7; ⊖ , run 4. (OH^-): ▲ , run 7; △ , run 4.
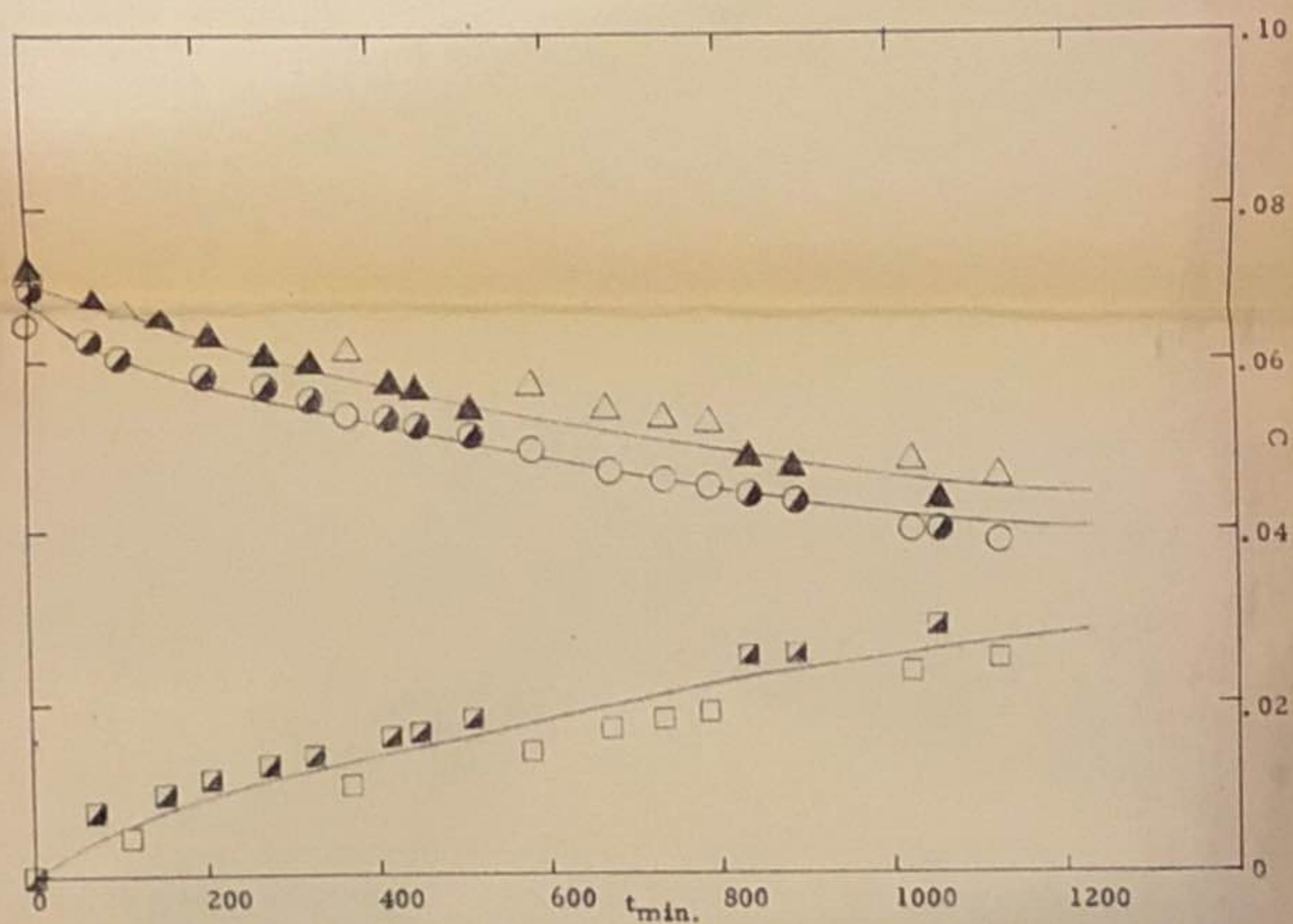
Fig. 7. Kinetics of the Solvolysis of n-Butyl bromide in the presence of Sodium hydroxide in 25% Methanol-75% Water (by weight) at 50° C. (Br⁻): ◪, run 5; ☐, run 6. (BuBr): ◐, run 5; ○, run 6. (OH⁻): ▲, run 5; △, run 6.
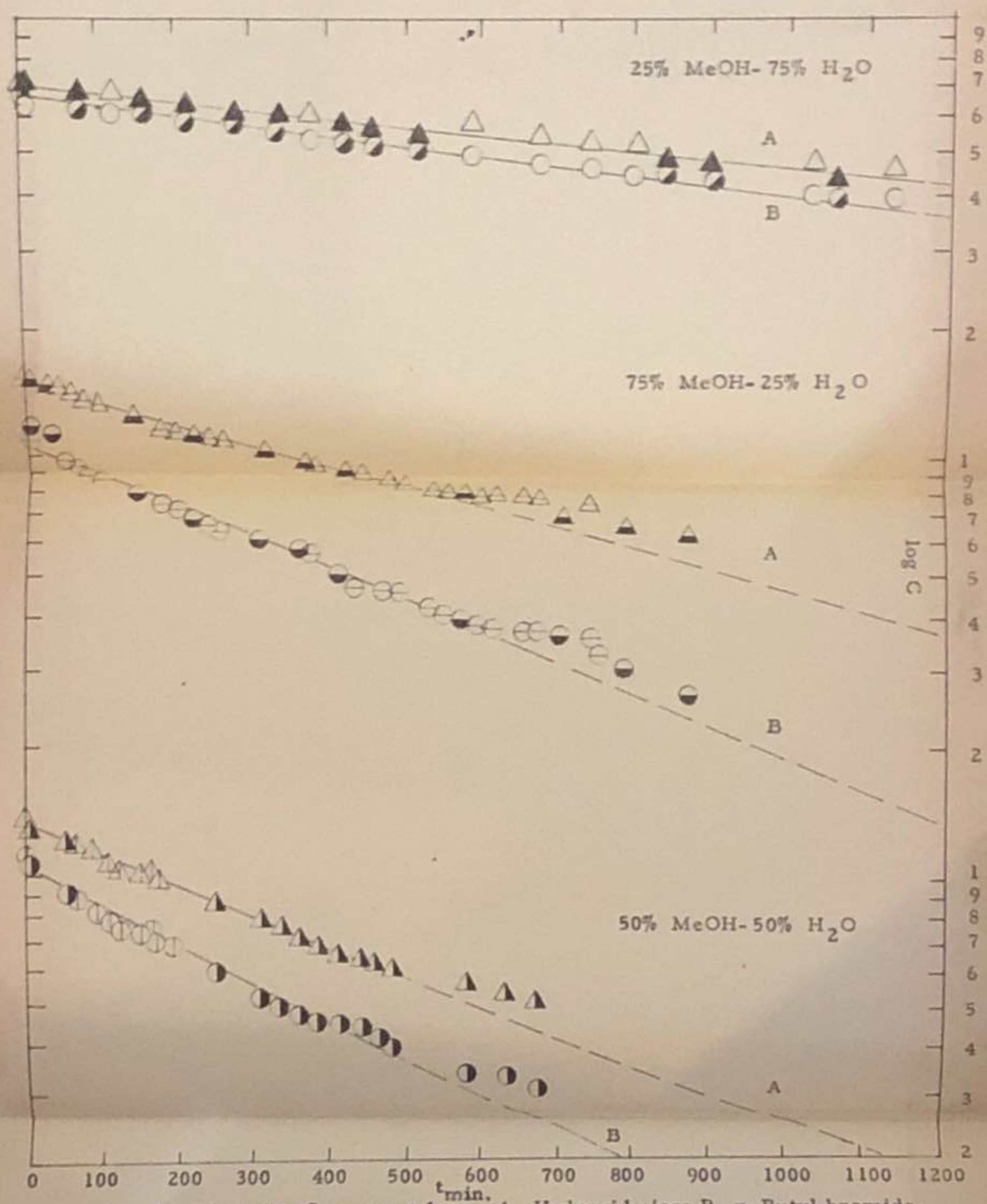
Fig. 8. Plot: log C versus t for: A, Hydroxide ion; B, n-Butyl bromide.
▲, ◐, run 5; △, ○, run 6; ◮, ◓, run 7; △, ◒, run 4; ◭, ◑, run 3;
△, ◐, run 2. (log C scale has been moved)

25% MeOH-75% H_2O

(OH⁻): ▲ , run 5; △ , run 6
(BuBr) ◗ , run 5; ○ , run 6

75% MeOH-25% H_2O

(OH⁻) ▲ , run 7; △ , run 4
(BuBr) ◓ , run 7; ⊖ , run 4

50% MeOH-50% H_2O

(OH⁻) ▲ , run 3; △ , run 2
(BuBr) ◗ , run 3; ◐ , run 2

(log C scale has been moved)

$t_{min.}$

0   Fig. 9   100   200   300   400   500   600   700

log C
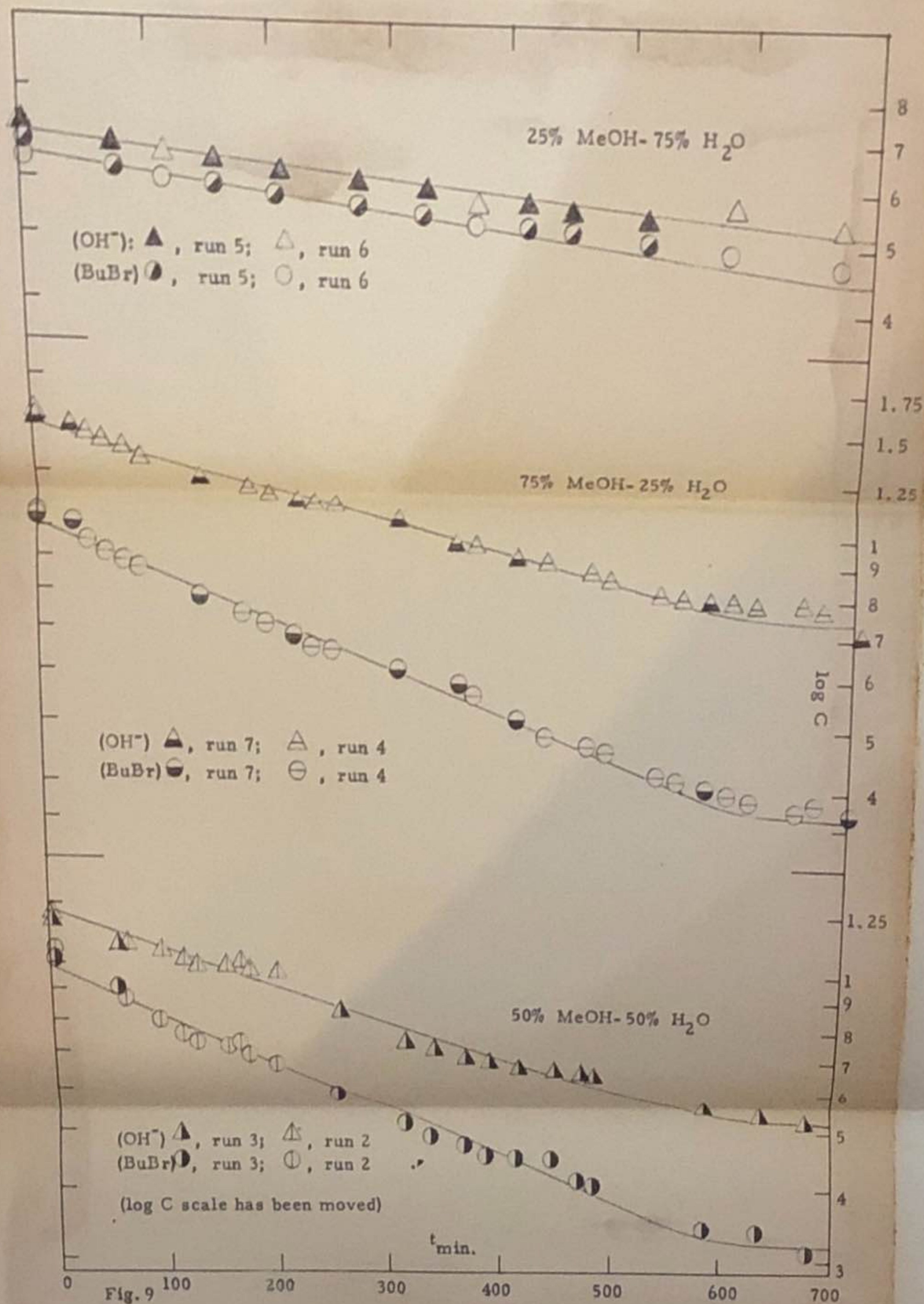
TABLE XIII

PER CENT REACTION SUMMARY *

Solvent		$t_{1/4}$		$t_{1/2}$		$t_{3/4}$		t	
		A	B	A	B	A	B	A	
50% MeOH		160	148	400	437	840	934	1540	[OH⁻]
		105	78	310	316	650	722	1140	[BuBr]
75% MeOH		220	230	590	647	1180	1363	2240	[OH⁻]
		140	169	380	382	780	863	1360	[BuBr]
25% MeOH		570	640	1600	1649	3160	3552	4540	[OH⁻]
		480	467	1330	1642	2450	3496	3340	[BuBr]

* A values represent those from plots of log C versus t (in minutes), assuming ideality; B values represent those calculated from the k_s(least squares) equations.

TABLE XIV

SUMMARY OF SOLVOLYTIC RATE CONSTANTS

FOR n-BUTYL BROMIDE IN METHANOL-WATER MIXTURES AT 50°

Run 2	Run 3	Run 4	Run 7	Run 5	Run 6	k value
2.34×10^{-2}	2.44×10^{-2}	1.61×10^{-2}	1.61×10^{-2}	6.11×10^{-2}	8.41×10^{-3}	k_2
	2.39×10^{-2}		1.61×10^{-2}		(3.48×10^{-2})	avg.
2.13×10^{-3}	1.61×10^{-3}	1.23×10^{-3}	1.85×10^{-3}	5.80×10^{-4}	4.15×10^{-4}	$k_{1(a-x)}$
	1.86×10^{-3}		1.54×10^{-3}		4.98×10^{-4}	avg.
2.82×10^{-3}	2.11×10^{-3}	2.07×10^{-3}	1.86×10^{-3}	7.21×10^{-4}	4.73×10^{-4}	$k_{1(b-x)}$
	2.46×10^{-3}		1.96×10^{-3}		5.97×10^{-4}	avg.
	2.16×10^{-3}		1.75×10^{-3}		5.48×10^{-4}	k_1 avg.
3.69×10^{-2}	3.14×10^{-2}	2.04×10^{-2}	2.10×10^{-2}	1.24×10^{-2}	8.60×10^{-3}	k_2'
	3.42×10^{-2}		2.07×10^{-2}		1.05×10^{-2}	avg.

Runs 2-3:			Runs 4-7:		Runs 5-6:	
k_m	(a-x)	1.20×10^{-3}		9.63×10^{-4}		3.69×10^{-4}
	(b-x)	1.78×10^{-3}		1.49×10^{-3}		4.38×10^{-4}
	avg.	1.49×10^{-3}		1.23×10^{-3}		4.04×10^{-4}
k_s	(a-x)	1.40×10^{-3}		9.72×10^{-4}		3.78×10^{-4}
	(b-x)	1.71×10^{-3}		1.44×10^{-3}		3.75×10^{-4}
	avg.	1.56×10^{-3}		1.21×10^{-3}		3.76×10^{-4}
k_1	(a-x)	9.55×10^{-4}		9.24×10^{-4}		4.44×10^{-4}
	(b-x)	6.87×10^{-4}		6.32×10^{-4}		1.87×10^{-4}
	avg.	8.21×10^{-4}		7.78×10^{-4}		3.16×10^{-4}