

THE INFLUENCE OF SOLVENTS ON THE VELOCITY
OF FORMATION OF QUATERNARY AMMONIUM SALTS.

by

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N. Menschutkin (Zeit. physikal Chem., 1890, 5, 589) and in several later papers shows that the influence exercised by the solvent on the velocity of combination of tertiary bases and alkyl halides is very great.

The experiments which follow were made in order to test the validity of certain suggestions that have been advanced to explain the nature of the action of the solvent.

Patterson and Montgomerie (T., 1912, 101, 26) show that change of solvent frequently affects different reactions in the same order. From this, Cox (T., 1921, 119, 142) assumes that reactions take place by the formation of intermediate compounds or solvent-solute complexes, the velocity of reaction being dependent on the constitution of the complex, is also dependent on the constitution of the solvent and solute.

To test this assumption, freezing point curves of mixture of solvent and tertiary base and of solvent and alkyl halide were determined. Maas and MacIntosh/

MacIntosh (J.A.C.S., 34, 1278) and J. Kendall (J.A.C.S., 36, 1222) used this method for the examination of organic addition compounds. The molecular concentration is plotted against the temperature as on the addition of one pure substance to another pure substance, the melting points of both are lowered and two curves are obtained intersecting at their eutectic point. If a compound is formed it being a pure substance also, the further addition of either of the two former substances will lower its melting point and more than one eutectic point will be obtained.

Marcelin and Rice treating the problem of reaction velocity from the point of view of statistical mechanics correlate the velocity constant with the temperature. Rice (Brit. Ass. Rep., 1915, 397) shows that the relation between the velocity constant k and the absolute temperature is $\frac{d \log k}{dt} = \frac{E}{RT^2}$. This equation of Marcelin and Rice is identical with Arrhenius' equation $\log \frac{k t_1}{k t_2} = A \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ which agrees well with experimental data.

Lewis and Lamble (T, 1914, 105, 2330) deduce from Arrhenius' equation that "when a positive catalyst is present in large quantity a diminution of the temperature-coefficient should take place" and by applying/

applying the quantum theory to the Marcelin-Rice equation Lewis (T., 1916, 109, 796) draws the conclusion that "any agency which increases the reaction velocity diminishes the temperature-coefficient of the constant."

Lewis assumes that the critical energy increment, E , the quantity of energy necessary to make an average gram molecule react, is supplied by the absorption of infra red radiation of a given frequency which the substance is capable of absorbing. The radiation is present in the system by virtue of its temperature.

Temperature-coefficients and the value of E for the velocity of combination of pyridine and allyl bromide were obtained in order to investigate whether or not the influence exercised by the solvent is due to infra red radiation.

EXPERIMENTAL.

FREEZING POINT CURVES.

Freezing point curves were used to determine whether or not addition compounds were formed. Temperatures from $+10^{\circ}$ to -15° were obtained by using ice and salt, -15° to -70° by solid carbon dioxide and acetone, temperatures lower than -70°C .
by/

by the use of liquid air. The apparatus used resembled the usual Beckman apparatus. The outer tube was kept at a temperature slightly lower than the freezing point of the mixture in the inner tube, which was constantly stirred. The inner tube with the mixture to be examined was contained in a slightly larger, carefully dried glass tube. This was inserted in the bath of solid carbon dioxide and acetone or liquid air which was kept in an unsilvered Dewar flask. When the mixture had solidified the inner tube was transferred to a dry outer tube and placed in an empty Dewar flask to warm up slowly so that frostiness was avoided. The temperature was recorded when the first crystals appeared on lowering the temperature and again when the last crystals disappeared on raising the temperature.

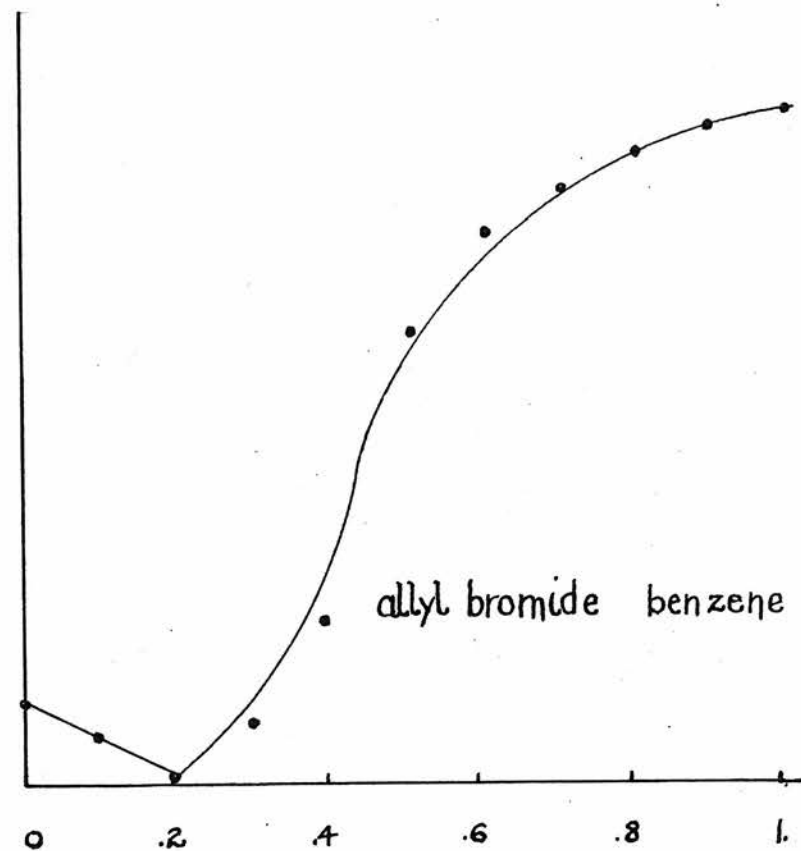
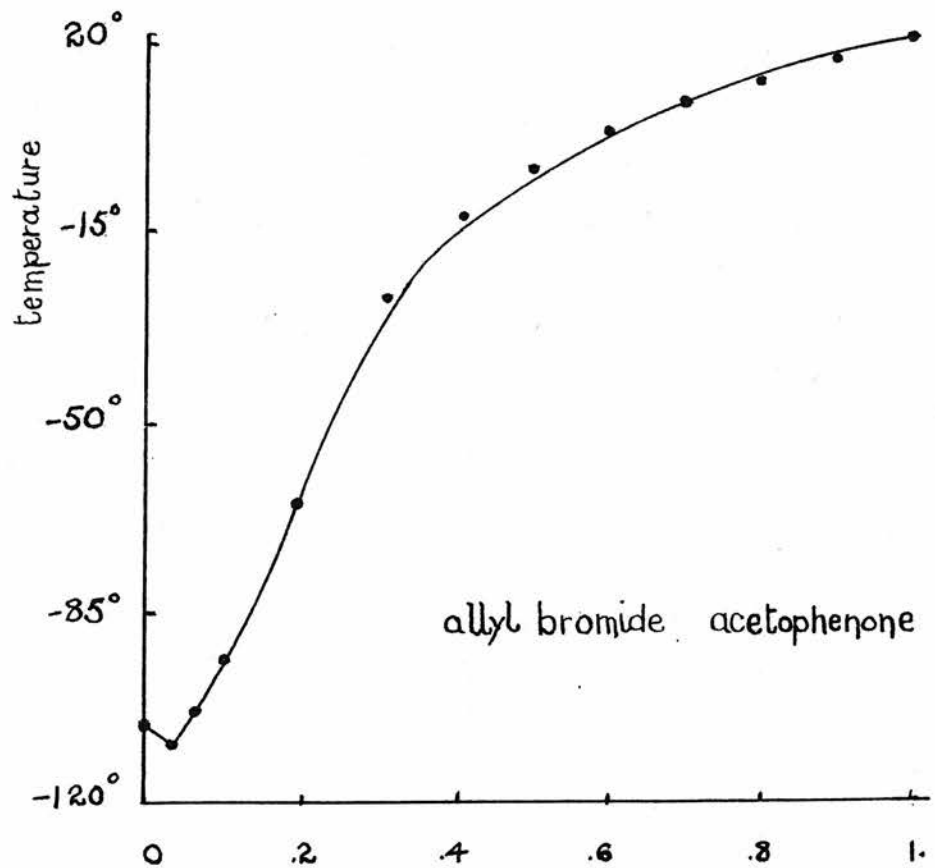
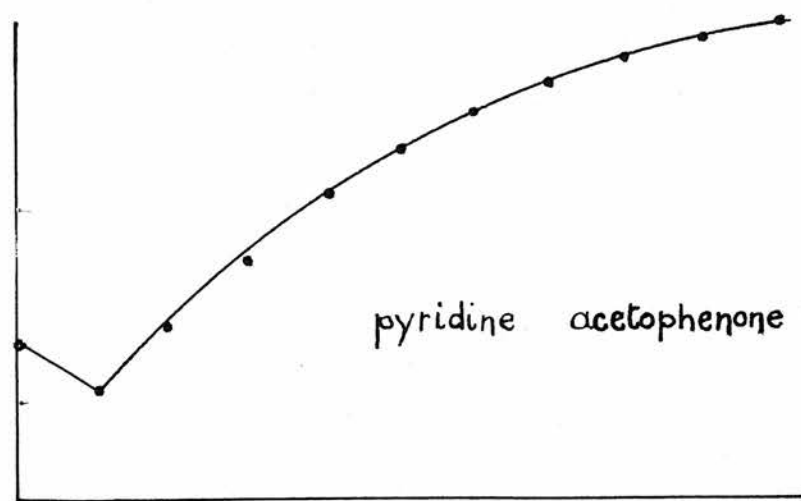
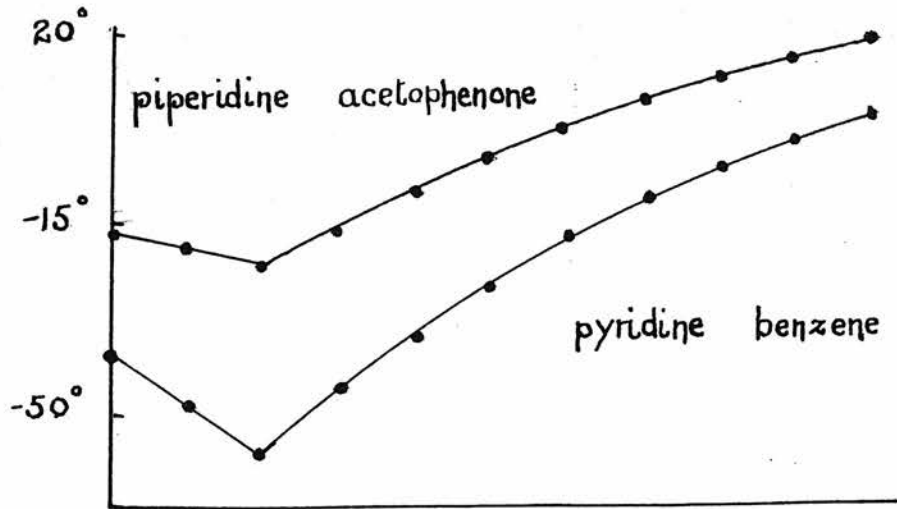
mol.) pyridine	1.	.9	.8	.7	.6	.5	.4	.3	.2	.1	0.
conc.) acetophenone	0.	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
melting point	- 42°	- 49°	- 36°	- 23°	- 12°	- 3°	+ 3°	+ 8°	+ 12°	+ 16°	+ 20°

mol.) pyridine	1.	.9	.8	.7	.6	.5	.4	.3	.2	.1	0.
conc.) benzene	0.	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
melting point	- 42°	- 49°	- 56°	- 46°	- 36°	- 28°	- 18°	- 12°	- 5°	+ 1°	+ 4°

mol.) allyl bromide	1.	.975	.9	.8	.7	.6	.5	.4	.3	.2	.1	0.
conc.) acetophenone	0.	.025	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
melting point	-106°	- 109°	- 94°	- 66°	- 25°	- 12°	- 3°	+ 3°	+ 8°	+ 12°	+ 16°	+ 20°

mol.) allyl bromide	1.	.9	.8	.7	.6	.5	.4	.3	.2	.1	0
conc.) benzene	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
melting point	- 106°	- 110°	- 120°	- 110°	- 92°	- 37°	- 17°	- 12°	- 4°	+ 2°	+ 4°

mol.) piperidine	1.	.9	.8	.7	.6	.5	.4	.3	.2	.1	0
conc.) acetophenone	0	.1	.2	.3	.4	.5	.6	.7	.8	.9	1.
melting point	- 17°	- 20°	- 22°	- 18°	- 8°	- 3°	+ 1°	+4.5°	+11°	+15°	+ 20°



molecular concentration

When these numbers are plotted curves are obtained which in all cases have only one eutectic point. (Fig. I.) Consequently no addition compounds were detected either in the case of mixtures of the tertiary base and the solvent or in mixtures of the alkyl halide and solvent. The two solvents chosen were as diverse as possible, the reaction proceeding very rapidly in acetophenone and very slowly in benzene. The freezing point curve of piperidine and acetophenone was also determined as although piperidine is a secondary base its reaction with allyl bromide proceeds much more rapidly than the reaction of pyridine and allyl bromide.

From this, it would appear that the reaction does not take place by the formation of intermediate compounds or solvent-solute complexes, consequently the velocity of reaction cannot be determined by these solvent-solute complexes.

REACTION VELOCITIES.

Solutions of pyridine and allyl bromide in different solvents were prepared and sealed in glass tubes, the resulting solution being .37 N with respect to both reactants. The quaternary ammonium salt precipitated out as a heavy red oil in all solvents except alcohol. The weight of the mixture in each tube was determined and the tubes immersed in a thermostat, temperatures used being 28.3°C., 38.3°C., and 56.5°C. A tube was withdrawn at intervals and broken into a white porcelain dish containing cold distilled water and was titrated with silver nitrate, using potassium chromate as an indicator. Time was taken in minutes and reckoned from the withdrawal of the first tube from the thermostat, a few minutes after immersion. The velocity of reaction was calculated by the formula

$$k = \frac{1}{C_0 t} \cdot \frac{C_t}{C_0 - C_t}$$

All the solvents and reactants were carefully purified and dried as efficiently as possible. The alcohol was placed over calcium oxide and allowed to stand, finally refluxed over metallic calcium and distilled. Alcohol 99.8% absolute was obtained.

Solvent toluene Temperature 28.5°C.

time	C_t %	k
1146	9.16	.000235
1183	9.33	.000235
1273	10.30	.000243

benzene

time	C_t %	k
1115	11.20	.000305
1183	12.12	.000312
1589	16.27	.000316

alcohol

time	C_t %	k
65	6.74	.00299
95	8.55	.00254
193	15.81	.00253

acetone

time	C_t %	k
121	19.36	.00503
161	23.78	.00502
197	27.68	.00508

p nitrotoluene

time	C_t %	k
172	30.46	.00659
192	32.61	.00653
245	38.37	.00658

acetophenone

time	C_t %	k
178	41.05	.01013
227	46.00	.01014
253	50.90	.01061

nitrobenzene

time	C_t %	k
107	34.41	.0127
140	41.48	.0131
202	46.84	.0114

toluene

temperature 38.3°C.

time	C_t %	k
243	4.22	.000489
270	4.70	.000475
280	5.11	.000518

benzene

time	C_t %	k
188	4.05	.000640
207	4.92	.000647
275	6.63	.000655
285	6.74	.000656
353	8.13	.000650

alcohol

time	C_t %	k
120	21.17	.00557
210	30.59	.00551
245	35.09	.00568

acetone

time	C_t %	k
44	14.04	.00959
54	16.75	.00966
65	16.89	.00964
180	39.82	.00950

p. nitrotoluene Temperature 37°C.

time	C_t %	k
51	15.70	.00944
109	33.12	.01150
127	36.73	.01185

acetophenone Temperature 38.3°C.

time	C_t %	k
152	55.19	.0209
190	59.46	.0200
202	60.85	.0199

nitrobenzene Temperature 37°C.

time	C_t %	k
53	31.90	.0229
71	39.38	.0236
84	43.42	.0237

Temperature 56.5°C.

toluene

reactants .79 N.

time	C_t %	k	time	C_t %	k
87	5.88	.00186	162	19.28	.00186
117	8.12	.00195	190	22.59	.00193
			331	77.78	.00177

benzene			reactants .63 N.		
time	C_t %	k	time	C_t %	k
74	7.19	.00240	31	4.28	.00229
109	8.12	.00220	59	7.73	.00225
			109	13.53	.00227
alcohol			acetone reactants .79 N.		
time	C_t %	k	time	C_t %	k
25	16.32	.0201	30	43.49	.0328
55	31.54	.0202	61	60.35	.0338
66	33.75	.0208	95	71.65	.0337
p. nitrotoluene			acetophenone reactants .56 N.		
time	C_t %	k	time	C_t %	k
15	17.85	.03759	11	23.95	.0519
36	34.41	.03769	17	32.81	.0514
			28	45.27	.0532
acetophenone					
time	C_t %	k			
20	28.87	.0526			
solvent nitrobenzene					
time	C_t %	k			
86	73.71	.0845			
96	75.84	.0847			
125	80.49	.0854			

These results are tabulated below.

Solvent/

Solvent.	k temperature		
	28.3°C.	38.3°C.	56.5°C.
toluene	.000231	.000517	.00186
benzene	.000305	.000642	.00223
alcohol	.00251	.00557	.0202
acetone	.00505	.0102	.0338
p. nitrotoluene	.00657	.0126	.0376
acetophenone	.0104	.0203	.0526
nitrobenzene	.0129	.0251	.0848

There is a very marked difference in the velocity of reaction in these solvents, being over forty times faster in nitrobenzene than in toluene.

MIXED SOLVENTS.

Allyl bromide and pyridine were added in the same concentration to mixtures of two solvents and the reaction velocities determined.

Molecular concentration.		temperature 56.5°C.		
Solvents	acetone	toluene		
	1	0	.0338	
			reactants .79 N	
	0.88	.012	time	C _t % k.
			27	32.50 .0226
			43	49.56 .0289
			159	75.09 .0239

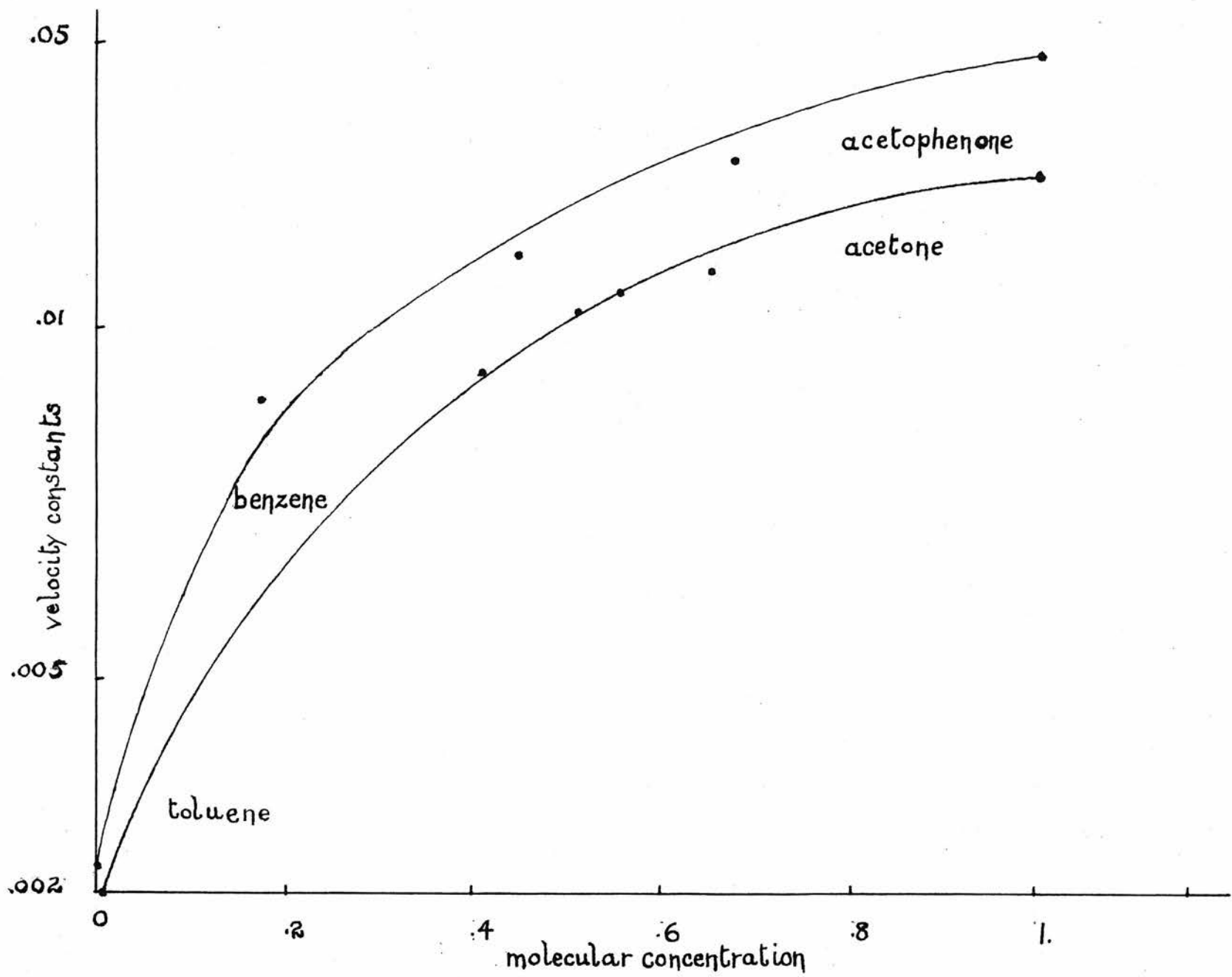
Molecular concentration.

Solvents

acetone	toluene	time	C_t %	k
0.75	0.25	48	40.57	.0180
		112	60.87	.0176
		152	67.16	.0171
		time	C_t %	k
0.59	0.41	152	60.80	.0129
		190	66.00	.0129
		223	68.59	.0129
		time	C_t %	k
0.4	0.6	80	37.31	.00936
		100	41.84	.00918
		time	C_t %	k
0.23	0.77	30	13.01	.00709
		64	23.06	.00667
0	1.			.00193

Solvents

acetophenone	benzene	reactants	.63 N.	k
1	0			.0526
		time	C_t %	k
0.68	0.32	10	17.38	.0360
		15	25.43	.0333
		37	44.09	.0338
		time	C_t %	k
0.43	0.57	29	26.26	.01956
		39	33.22	.0202
		73	48.69	.0206



Molecular concentration.

Solvents

acetophenone	benzene	time	C_t %	k
0.19	0.81	10	5.43	.00911
		29	14.31	.00914
		76	27.89	.00806
				k
0	1.			.00227

When the molecular concentration of the two solvents is plotted against the reaction velocity (Fig. II) it is seen that the curve does not fall off in a straight line from the highest to the lowest velocity, but falls slowly until a concentration is reached where the solvent in which the reaction takes place more slowly predominates to a very great extent and then drops rapidly.

From this, it appears that the solvent in which the reaction proceeds more rapidly has a greater effect on the reaction velocity than corresponds to its concentration.

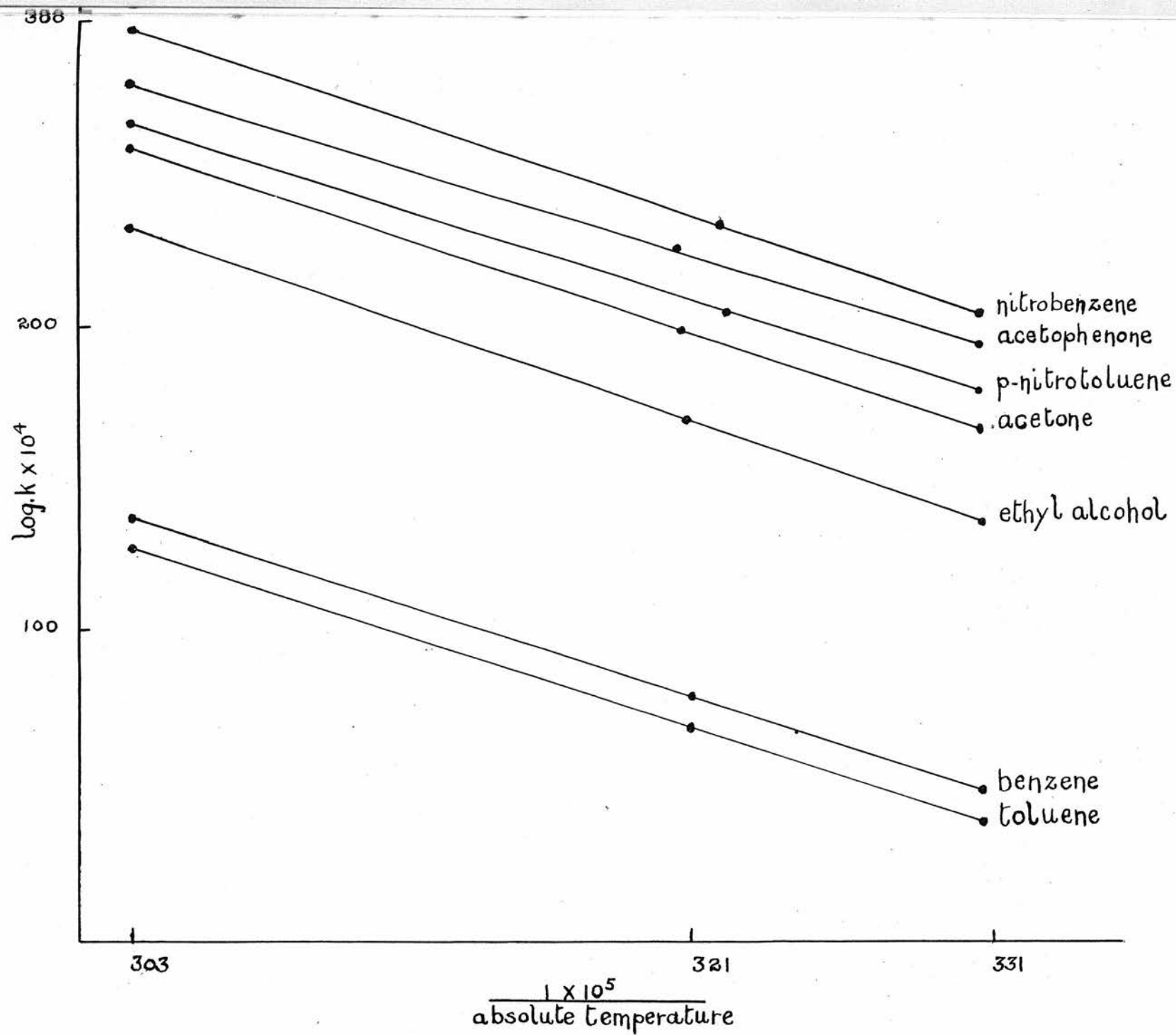
TEMPERATURE-COEFFICIENTS.

The usual form of expressing temperature-coefficients is by the ratio $\frac{k_t + 10}{k_t}$. The values of this ratio over the range 28.3°C. to 56.5°C. are given in the following table.

Solvent	$\frac{k_{38.3^\circ}}{k_{28.3^\circ}}$	$\frac{k_{56.5^\circ}}{k_{38.3^\circ}}$	$\frac{k_{56.5^\circ}}{k_{28.3^\circ}}$	$\frac{k_t+10}{k_t}$ for	$\frac{k_{56.5^\circ}}{k_{28.3^\circ}}$
toluene	2.25	3.59	8.05	1.97	
benzene	2.11	3.47	7.31	1.90	
alcohol	2.21	3.62	8.04	1.98	
acetone	2.02	3.31	6.70	1.82	
p. nitro- toluene	1.92	2.98	5.72	1.63	
aceto- phenone	1.95	2.59	5.06	1.42	
nitro- benzene	1.94	3.37	6.57	1.85	

From these results it is seen that the value per degree of temperature for the ratio $\frac{38.3^\circ}{28.3^\circ}$ is slightly higher than for the ratio $\frac{56.5^\circ}{38.3^\circ}$ which agrees with Lewis' theory that "any agency which increases the reaction velocity diminishes the temperature-coefficient of the constant."

The results are shown to agree with the integrated formula of Arrhenius or of the radiation theory by the graph (Fig. III) in which the logarithm of/



of the velocity constant is plotted against the reciprocal of the absolute temperature within the limit of experimental error. The slope of the line indicates the temperature-coefficient.

The effect of the temperature on the velocity is better expressed by the term E , denoting the difference between the critical energy and the mean internal energy reckoned per gram molecule, assuming that a molecule reacts when its internal energy has been raised to a certain critical value, which is generally large compared to the average internal energy of the molecule. E represents the amount of energy per average gram molecule necessary in order that the reaction may proceed.

$$\log k_{t_2} - \log k_{t_1} = \frac{E}{R} \left(\frac{1}{t_1} - \frac{1}{t_2} \right)$$

$$R = 1.985 \text{ calories.}$$

The following are the mean values of E for this reaction.-

Solvent	E	k 28.3°C.
toluene	15,100	.000231
benzene	14,400	.000305
alcohol	15,100	.00251
acetone	13,600	.00505
p. nitrotoluene	12,600	.00657
acetophenone	12,100	.0104
nitrobenzene	13,300	.0129

E in these results is in the inverse order to the velocity of the reaction except in the case of alcohol and nitrobenzene. All the other results are in agreement with the conclusion of Lewis and Lamble, "that any agency which increases the velocity of the reaction diminishes the temperature-coefficient of the velocity constant". The temperature-coefficient is not inversely proportional to the reaction velocity in different solvents, so other influences besides that of radiation alone must control the velocity of the reaction.

Attempts were made to find a connection between reaction velocity and the viscosity of the medium, but these were unsuccessful as in this reaction, the reaction velocities are very different in media of nearly the same viscosity. There is a rough agreement between the dielectric constants and the reaction velocities, the reaction velocities generally increasing in the same order as the dielectric constants of the solvents.

Solvent	k 28.3°C	viscosity 26°C	dielectric constant
toluene	.000231	.0053	2.31
benzene	.000305	.0060	2.26
alcohol	.00251	.0109	25.8
acetone	.00505	.003	21.5
aceto-phenone	.0104	.019	18.1
nitro-benzene	.0129	.018	36.5

The values of the viscosity and dielectric constants of the solvents were taken from the Landolt Bornstein Tables except in the case of the viscosity of acetophenone which was determined with reference to benzene.

In the case of alcohol and nitrobenzene where the temperature-coefficients of the velocity constants are abnormally high, the dielectric constants are also abnormally high.

S U M M A R Y.

Freezing point curves of mixtures of solvent and reactants have been constructed. No addition compounds were detected. The influence of the solvent is therefore not due to addition compounds or solvent-solute complexes.

The temperature-coefficients of the reaction have been determined in a number of different solvents. The value of the temperature-coefficient per degree of temperature for the ratio $\frac{38.3^{\circ}}{28.3^{\circ}\text{C.}}$ is slightly higher than for the ratio $\frac{56.5^{\circ}}{38.3^{\circ}\text{C.}}$ which agrees with Lewis' theory.

The mean value of E in different solvents has been determined. E is in the inverse order to the velocity/

velocity of the reaction, except in the case of alcohol and nitrobenzene, which also agrees with Lewis' theory "that any agency which increases the velocity of the reaction diminishes the temperature-coefficient of the velocity constant".

The temperature-coefficient is not inversely proportional to the reaction velocity in different solvents, so other influences besides that of radiation alone must control the reaction velocity.

There is a rough agreement between the dielectric constants and the reaction velocities.
