16. *Kinetics of the Reaction between Ethylene Glycol and Lead Tetra-acetate.*

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The kinetics of the reaction between lead tetra-acetate and ethylene glycol have been investigated in acetic acid solution between 18° and 45°. The reaction is of the first order with respect to each reactant and obeys the Arrhenius equation with a steric factor of approximately unity. It is suggested that the occurrence of this high steric factor in a reaction between two uncharged molecules is associated with a mechanism involving free radicals rather than ions.

Lead tetra-acetate has been widely used for oxidising glycols quantitatively to two molecules of aldehyde. Kinetic measurements on this type of reaction have been made by Criegee (*Ber.*, 1931, **64**, 260) and Criegee, Craft, and Rank (*Annalen*, 1933, 507), but only two temperatures differing by 10° were used and the initial concentrations were not systematically varied. We have now investigated the order of the reaction and the temperature coefficient for the reaction between ethylene glycol and lead tetra-acetate in acetic acid solution.

EXPERIMENTAL.

Lead tetra-acetate was prepared by shaking red lead with glacial acetic acid, warming the mixture to 35°, and saturating it with chlorine. It was recrystallised from glacial acetic acid, and its purity checked by titrating the iodine liberated from potassium iodide. Ethylene glycol was fractionally distilled. Acetic acid was purified by partly freezing several times. Further fractional freezing had no effect upon the velocity, though the addition of small quantities of water caused a marked increase, and it was necessary to exclude moisture carefully in the kinetic measurements.

The reaction was followed by adding samples to potassium iodide, filtering off the lead iodide, and titrating the iodine liberated with N/400-thiosulphate solution.

Results.—In all the experiments the concentration of ethylene glycol was at least ten times that of lead tetra-acetate, and the course of each reaction was of the first order within the experimental error. This is illustrated by the data for a typical experiment given in Table I.

TABLE I.

18°; 0·125M-glycol; 0·0125M-lead tetra-acetate. 2 C.c. of reaction mixture added to 5 c.c. of KI solution, lead iodide filtered off, and 5 c.c. of filtrate titrated.

Time, mins.	5	15	25	35	55	75	95	115	135	155
Titre, c.c. obs.	12·1	11·3	10·6	10·1	9·1	8·1	7·3	6·5	6·0	5·4
Titre, c.c. calc.	11·9	11·3	10·7	10·1	9·1	8·1	7·2	6·5	5·8	5·2

The calculated values of the titre (x) are given by $\log_{10}x = 1{\cdot}087 - 0{\cdot}00238t$.

Table II contains a summary of the results obtained. The first-order constants k_1 are expressed in decadic logarithms, and were obtained by plotting the logarithm of the titre against the time. The bimolecular constants k_2 are given by $k_2 = 2{\cdot}30k_1/c$, where c is the concentration of ethylene glycol in g.-mols./l. The time is in minutes throughout.

TABLE II.

c.	$100k_1$.	$100k_2$.	c.	$100k_1$.	$100k_2$.	c.	$100k_1$.	$100k_2$.	c.	$100k_1$.	$100k_2$.
	At 18°.			At 25°.			At 35°.			At 45°.	
0·125	0·238	4·4	0·125	0·55	10·1	0·125	1·78	33	0·125	4·49	83
0·100	0·162	3·7	0·125	0·48	9·2	0·125	1·72	32	0·100	3·41	79
0·075	0·099	3·0	0·100	0·35	8·1	0·125	1·62	30	0·075	2·75	85
0·050	0·060	2·7	0·083	0·42	11·5	0·083	1·02	30		**Mean**	82
0·050	0·082	3·8	0·075	0·265	8·1	0·083	1·06	31			
0·025	0·032	2·9	0·050	0·148	6·8	0·050	0·63	29			
	Mean	3·4	0·025	0·067	6·1		Mean	31			
				Mean	8·5						

DISCUSSION.

The above results show that the reaction is of the first order with respect to each of the two reactants within the rather low experimental accuracy. If the glycol concentration is raised much above 0·125M, the bimolecular constants tend to rise above the values obtained with lower concentrations, but the above figures show that a five-fold variation below 0·125M does not cause any trend in the constants.

The bimolecular constants at the different temperatures obey the Arrhenius equation within the experimental error, as shown by the following data, where the calculated values are given by $k_2 = 1{\cdot}95 \times 10^{14}e^{-20,900/RT}$.

Temp.	18°	25°	35°	45°
$100k_2$ obs.	3·4	8·5	31	82
$100k_2$ calc.	3·7	8·7	28	82

These results are in essential agreement with those of Criegee (*loc. cit.*), who found an activation energy of 22,200 cals. from measurements at 20° and 30°. The probable error in the activation energy is about 1000 cals., so the non-exponential factor of the Arrhenius equation does not differ significantly from the value of about 5×10^{13} predicted by the simple collision theory. The same is true of the majority of the other glycols studied by Criegee. This reaction appears to be the first example of a reaction between two uncharged molecules in solution for which the steric factor is approximately unity. The other reactions between uncharged molecules which have been investigated have an ionic mechanism, and the low values of the steric factor associated with them are probably due to the orientation of solvent molecules round a polar critical complex. It is reasonable therefore to suppose that the high steric factor found in the present case is due to the occurrence of a radical rather than an ionic mechanism, and this idea is supported by chemical evidence (compare Waters, J., **1939**, 1805).

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