88. *The Oxidation of Cyclic Compounds by Potassium Permanganate.*

By C. N. HINSHELWOOD and C. A. WINKLER.

WIDELY different rates are observed for the oxidation of various phenols with potassium permanganate, under conditions where kinetic experiments indicate that the rate-determining process is the initial rupture of the ring (Hinshelwood, J., 1919, **115**, 1180). Except for picric acid (Musgrave and Moelwyn-Hughes, *Trans. Faraday Soc.*, 1933, **29**, 1162), the energies of activation have not hitherto been determined. In order to obtain information about the probability factor P in the expression, rate $= PZe^{-E/RT}$, the temperature coefficients have now been determined for a series of such oxidation reactions.

5 C.c. of $N/10$-potassium permanganate solution and 5 c.c. of a solution of the organic compound in dilute sulphuric acid (usually 0·02N) were sealed in glass tubes and allowed to react for measured periods of time. The reaction was stopped by emptying the contents of the tube into potassium iodide solution. Oxides of manganese are precipitated during the reaction and adhere to the sides of the tube, but can be removed by potassium iodide acidified with sulphuric acid. The iodine liberated was titrated with sodium thiosulphate.

Under the conditions of the experiments, the permanganate had only three-fifths of its nominal oxidising power, so the concentration of each solution to be oxidised was chosen so as to be just sufficient for reaction with an equal volume of the permanganate; *i.e.*, the concentration was $0{\cdot}03m/n$ g./l., where n = number of atoms of oxygen required for the complete oxidation of 1 g.-mol. to carbon dioxide, water, and, in the case of nitro-compounds, nitric acid, and m is the molecular weight. (In all cases the complete oxidation occurred more rapidly than the initial step.)

All the organic compounds were recrystallised to constant m. p., thermometers were compared with N.P.L. standards, and blank experiments were made to show that the amount of decomposition which potassium permanganate undergoes by itself under the conditions of the experiments was negligible.

The rate of reaction in most cases can be expressed by the equation $dx/dt = k(a - x)(b - cx)$, where a and b are the initial concentrations of the organic compound and of the permanganate respectively, both in *g.-mols. per l.*, and c is the number of mols. of permanganate used in completely oxidising 1 mol. of the organic compound. With the above concentrations, $a = b/c$; hence $dx/dt = kc(a - x)^2 = k_0(a - x)^2$, and k_0 can be calculated from the percentage change and the time. If, however, we assume that the primary process is a collision between a permanganate ion and a molecule of the organic compound, then we must, for any calculations of molecular statistics, use k, which is given by

$$k_0 \times \text{(concn. of organic substance)/(concn. of permanganate)}$$

When mixed with the other reactant, the permanganate was 0·05N, *i.e.*, $M/100$, so that

$$k = k_0 \times \text{(concn. of organic substance)} \times 100.$$

With most of the compounds used, the bimolecular formula is fairly well satisfied, though in some cases a trend appears. Three examples are given in Table I. There is no induction period, nor, in general, any autocatalysis which would suggest complex mechanisms analogous to those found in the reaction between potassium permanganate and oxalic acid.

TABLE I.

(k is expressed in g.-mol./l./sec.)

Picric acid; 25°.			*m*-Dinitrobenzene; 60°.			Benzoic acid; 60°.		
$a = 1{\cdot}07 \times 10^{-3}$.			$a = 1{\cdot}00 \times 10^{-3}$.			$a = 1{\cdot}00 \times 10^{-3}$.		
Mins.	Change, %.	$k \times 10^2$.	Mins.	Change, %.	$k \times 10^3$.	Mins.	Change, %.	$k \times 10^3$.
16	11·2	1·31	60	20·4	7·1	92	10·6	2·1
46	26·9	1·33	126	35·0	7·1	247	18·8	1·6
71	36·2	1·33	241	51·0	7·2	400	28·8	1·7
92	40·6	1·24	363	61·2	7·2	824	44·4	1·6
144	50·6	1·19	432	66·2	7·5	837	45·0	1·6
						1347	59·4	1·8
						1913	67·5	1·8

For the two dinitrophenols, the formula does not hold, but a slight autocatalytic effect appears. Values of k for the primary interaction were calculated from the initial rates, which fortunately could be determined quite accurately, since the reaction–time curves for the two compounds are nearly linear over the first third of their course.

Table II gives the constants at various temperatures, and Table III the values of the activation energies, and of log ($k_{100^\circ} \times 10^7$), k_{100° being the calculated value of k at 100°.

DISCUSSION.

Before any attempt is made to correlate log k and E, we must consider what agent is responsible for the oxidation. The simplest assumption is that the primary ring-breaking step is an interaction of a permanganate ion with a molecule of the organic compound.

TABLE II.

Picric acid.		2 : 4 : 6-Trinitro-*m*-cresol.		2 : 4-Dinitrophenol.		2 : 6-Dinitrophenol.	
t.	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.	*t.*	$k \times 10^3$.
15·0°	6·4	25·0°	1·58	0·0°	0·50	0·0°	10·5
25·0	12·8	40·0	5·06	15·6	2·12	15·6	49·6
40·0	35·8	60·0	19·2	25·0	5·06	25·0	119
60·0	115	80·4	82	40·0	18·5	40·0	417

Benzoic acid.		*m*-Dinitrobenzene.		2 : 4 : 6-Trinitro-3-methylnitroaminophenol.	
t.	$k \times 10^4$.	*t.*	$k \times 10^5$.	*t.*	$k \times 10^4$.
25·0°	1·97	25·0°	7·71	25·0°	8·3
40·0	5·54	40·0	31·2	40·0	25·8
60·0	17·9	60·0	167	60·0	89
80·0	58·3	80·0	717	80·4	282

TABLE III.

	E.	$\log_{10} (k_{100^\circ} \times 10^7)$.
Picric acid	12,200 *	6·90
Benzoic acid	12,700	5·15
2 : 4 : 6-Trinitro-3-methylnitroaminophenol	13,100	5·90
Trinitro-*m*-cresol	14,600	6·36
2 : 4-Dinitrophenol	15,300	6·98
2 : 6-Dinitrophenol	15,600	8·41
m-Dinitrobenzene	17,300	5·42

* For picric acid, Musgrave and Moelwyn-Hughes (*loc. cit.*) found 12,350 cals.

This is followed by faster reactions which lead to the complete oxidation of the products of ring breaking.* It is difficult to explain the apparently simple second-order course of most of the reactions on any other basis. We must also answer the question whether the organic compounds react as molecules or ions. Since picric acid, trinitrocresol, and 2 : 4 : 6-trinitro-3-methylnitroaminophenol are almost completely ionised in aqueous solution, and since it has been shown that the rate of reaction of picric acid is almost independent of the acidity of the solution, there can be little doubt that the ions themselves react. *m*-Dinitrobenzene does not ionise, and must therefore react as molecules.

Special experiments were made to determine whether benzoic acid and the dinitrophenols react as molecules or ions. The rate of reaction was measured in solutions of sulphuric acid of 0·05, 0·02, and 0·01*N* concentration. For benzoic acid and 2 : 4-dinitrophenol the rates in the first two solutions were the same, but that in the third was slightly smaller. Hence, it follows that the molecules are the main reacting species, and since, in determining the activation energy, the acid concentration was such that the reaction rate had attained its limiting value, we may use the bulk concentration as that of the reacting species without any correction for change of ionisation with temperature. With 2 : 6-dinitrophenol the situation is not quite so satisfactory : the rate of oxidation increased with increasing sulphuric acid concentration up to *N*/10. This means that molecules rather than ions react, but it also means that a small correction should be applied for change of degree of ionisation with temperature. On the other hand, the small correction would probably not very seriously affect the value 15,600 cals. for the activation energy.

When log *k* is plotted against *E*, a considerable variation in the *P* values becomes evident, and the influence of the structure of the organic compound on *P* appears as a very specific one.

Since these results are included in a general statistical survey of bimolecular reactions in the following paper, no further comments need be made here.

SUMMARY.

The activation energies for the oxidation of a number of cyclic compounds by potassium permanganate have been determined for use in a statistical survey of bimolecular reactions.

PHYSICAL CHEMISTRY LABORATORY, BALLIOL COLLEGE AND TRINITY COLLEGE, OXFORD.

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* In the two cases where there is an apparent autocatalysis it is probably to be attributed to an inadequate velocity of the reactions succeeding the ring rupture.