

Figure 5. Graph of $\ln[R'(n\omega_0)]$ vs $n\omega_0$.

given in table 1. The tabulated values establish the validity of the technique. It may be observed that on an average the error does not exceed 8.2%.

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Ru(III) CATALYSED OXIDATION OF 1,3 BUTANDIOL BY PHENYLIODOSOACETATE. A KINETIC STUDY

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DIOLS have been subjected to oxidation by various oxidising agents both in the presence and absence of catalyst¹⁻³. In continuation of our earlier work⁴⁻⁶, We report in this present communication, some inter-

esting results of Ru(III) catalysed oxidation of 1,3 butandiol by phenyliodosoacetate (PIA).

All the chemicals were of BDH (AR) grade. Phenyliodoso-acetate (PIA) was prepared by the modified method of Boesken and Schneider⁷. Ru(III) chloride (Johnson Mathey, London) was standardized by the method of Horiuchi *et al*⁸. The progress of the reaction was monitored by estimating PIA at regular intervals of time iodometrically. The product in the case of 1,3 butandiol is identified to be 3-hydroxy butanal, confirmed from its hydrazone derivatives.⁹

Interestingly the kinetic orders in the case of 1,3 butandiol are strikingly different from those of other diols studied⁶. The reaction in the case of 1,3 butandiol is found to be first order in the oxidant as evident from a good linearity in the plot of $\log(\text{PIA})$ versus time upto 75% of reaction. The pseudo-first order rate constant K_{obs} is also found to be constant over a wide range of PIA concentration (table 1), whereas earlier we have observed a zero order dependence on oxidant in the Ru(III) catalysed oxidation of diols (ethyleneglycol, 1,2 propandiol and 1,4 butandiol) by phenyliodosoacetate⁶.

Table 1 Effect of varying [Oxidant]/[Substrate] on the reaction rate:

[HClO ₄] = 0.01 M, HOAc = 10% (v/v),		[Ru(III)] = 8.87 × 10 ⁻⁷ M, Temp. = 35°C.
10 ³ [PIA] M	10 ⁴ [S] M	10 ³ k ₁ min ⁻¹
0.222	10.0	44.47
0.462	10.0	42.77
0.733	10.0	44.51
1.000	10.0	43.10
1.53	10.0	44.50
0.50	5.00	42.97
0.50	10.02	42.77
0.50	20.04	44.59
0.50	50.10	42.75

A ten fold increase in the concentration of 1,3 butandiol does not affect the pseudo-first order rate constant (table 1), proving the order with respect to substrate to be zero, whereas a first order dependence on (substrate) has been observed by us in the Ru(III) catalysed oxidation of diols by phenyliodosoacetate⁶.

The pseudo-first order rate constants increase on increasing the concentration of Ru(III) (table 2). The plots of $\log k_{\text{obs}}$ versus $\log [\text{Ru(III)}]$ are linear with unit slopes. The effect of HClO₄ on the reaction rate is found to be independent (table 2). An increase in the

Table 2 Effect of varying $[Ru(III)]/[HClO_4]$ and solvent composition on the reaction rate:

[S] = 0.001 M,		[PIA] = 0.0005 M,	Temp. = 35°C.
$10^7 [Ru(III)]$ M	$[HClO_4]$ M	% of HOAc	$10^3 k_1$ min ⁻¹
4.43	0.01	10	22.31
8.87	0.01	10	42.77
17.74	0.01	10	84.29
35.48	0.01	10	161.2
8.87	0.005	10	42.78
8.87	0.02	10	42.06
8.87	0.04	10	42.04
8.87	0.01	10	42.77
8.87	0.01	20	65.94
8.87	0.01	30	96.15
8.87	0.01	40	123.4

proportion of acetic acid (solvent) increases the rate (table 2) pointing the reaction to be a positive ion-dipole type. In order to investigate the effect of pH and of neutral salts, the rate measurements were carried out at various concentrations of NaOAc and NaClO₄ in aqueous acetic acid medium. There is no appreciable effect on the rate. Hence it can be inferred that there is no acid catalysis. The effect of temperature has been studied and the activation parameters at 308° K are as follows,

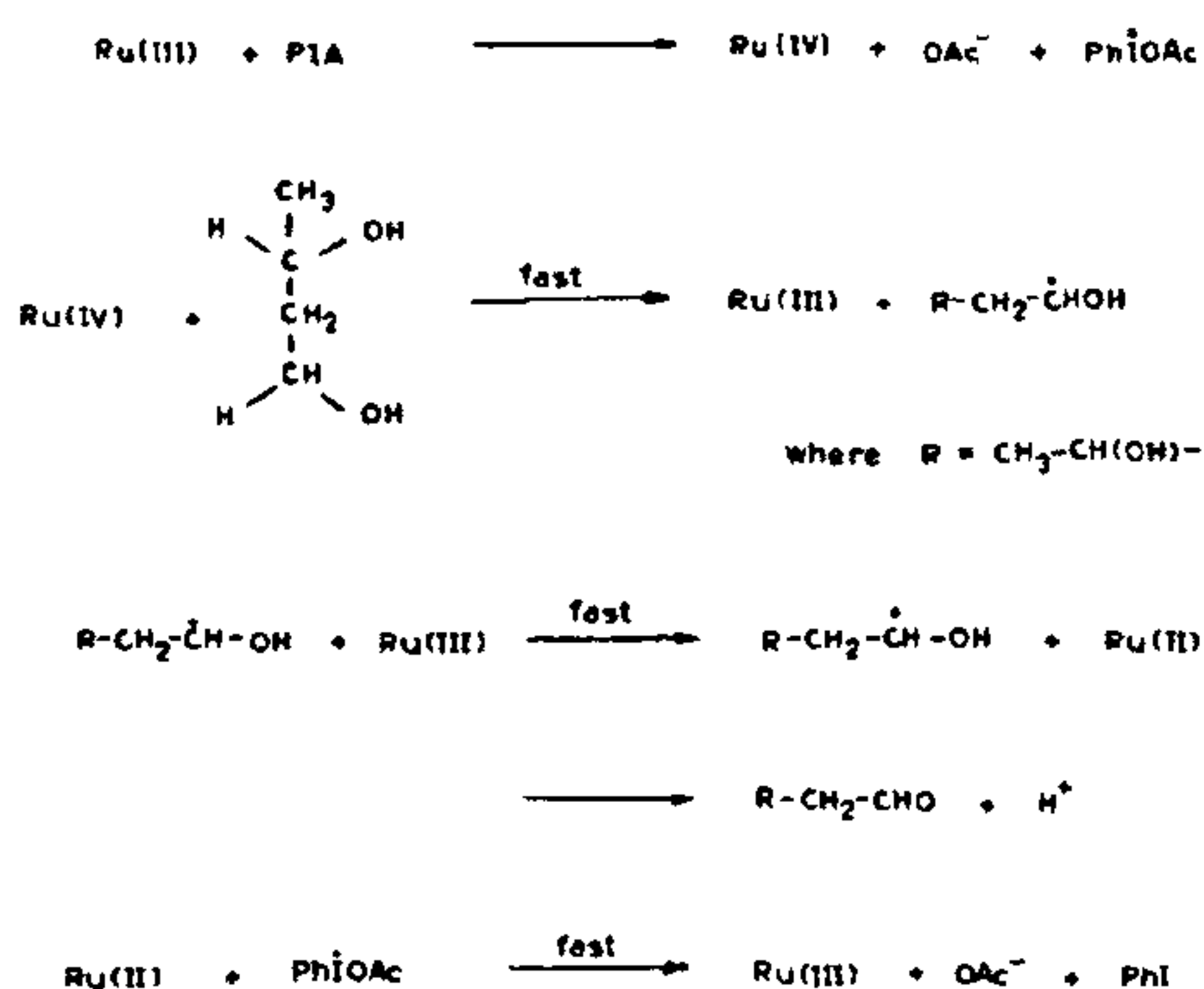
$$\Delta E = 18.31 \text{ K.cal/mole, } \Delta H^\ddagger = 17.70 \text{ K.cal/mole,}$$

$$\log_{10} A = 9.96 \text{ and } \Delta S^\ddagger = -15.05 \text{ e.u.}$$

Mechanism

The order in the substrate in 1,3-butandiol is found to be zero, which might arise due to the orientation of -OH group. The overcrowding of larger groups probably render its OH groups to be far apart and hence chelate formation is not favoured. The other possibility might be through an acyclic mechanism analogous to Ru(III) catalysed oxidation of diols and cyclanols as reported earlier by us⁶. But in the present case there being (a zero order in the substrate) this probability is also ruled out. An alternate approach might result from the generation of a higher valent species of Ru(III). Thus the reaction follows the sequence of steps shown in scheme I.

An immediate question then arises as to why such a mechanism does not operate in the other systems as reported earlier⁶. It appears that the rate of interaction of Ru(III) with the other diols like ethylene glycol, 1,2 propandiol and 1,4 butandiol as well as cyclanols (cyclopentanol, cyclohexanol, cycloheptanol and cy-



Scheme I.

cloctanol) is faster than the rate of interaction of Ru(III) with PIA. The former therefore rapidly occurs and the latter sequence of the reaction is suppressed. But in the case of 1,3 butandiol the rate of interaction of Ru(III) with PIA becomes faster than that of Ru(III) with the substrate. Hence the kinetic orders are changed and Ru(IV) generated as such reacts in a fast step with organic substrate. The evidence for the existence of Ru(IV) in aqueous medium is well documented¹⁰. The intermediacy of PhIOAc in PIA reaction has been invoked earlier by Pausacker *et al*¹¹.

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KINETICS OF THE ADDITION OF KETONES WITH 2,4-DINITROPHENYLHYDRAZINE

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THE addition of ketone with hydrazine is well known¹, but studies of kinetics of such reactions are very few² due to the rapidity of the reactions. The kinetics of the addition of acetone and ethylmethylketone, with 2,4-dinitrophenylhydrazine (DNPH) in aqueous acidic medium have therefore been studied for evaluating the kinetic parameters.

The reactions were comparatively fast and not amenable to conventional technique and hence a polarographic method was adopted^{3,4}. This was possible because DNPH yields diffusion current at DME while

acetone, ethylmethylketone and the product which precipitates out do not significantly do so.

Equimolar concentrations of the ketone and DNPH in 0.3 M sulphuric acid were mixed and the change in concentration of DNPH was followed from its diffusion current. Care was taken to presaturate the reaction system with the addition product so that the change in diffusion current with time truly represented the kinetics of the addition reaction. The concentration of unreacted DNPH at various time intervals during the reaction was estimated from a calibration curve obtained by measuring the galvanometer deflections with known concentrations of DNPH in the solution presaturated with the addition product. The DME was adjusted to yield precisely 24 drops per minute and the diffusion current at every fourth drop (*i.e.* interval of 10 sec) was recorded. From the readings (table 1) $1/[DNPH]$ versus time was plotted and the curve was linear indicating that the reaction was of the second order⁵. The slope of the curve evaluated by least square analysis showed a specific reaction rate. The kinetic studies with non-equimolar concentrations of the reactants confirmed these findings. Repeated trials yielded results agreeing to within 3%. Similar studies were carried out at various temperatures and the activation parameters were evaluated. The effect of acidity and solvent composition on the specific rate was also investigated.

Table 1 The kinetics of addition of acetone and DNPH in 0.3 M sulphuric acid

Time (t/sec)	Deflection (d/cm)	Conc. of unreacted DNPH/ 10^{-3} M	$\frac{1}{[DNPH]}/10^2$ M ⁻¹
0	21.9	3.00	3.33
20	20.5	2.81	3.56
30	19.8	2.71	3.69
40	19.3	2.64	3.78
50	18.7	2.56	3.90
60	18.2	2.49	4.01
70	17.7	2.42	4.12
80	17.2	2.36	4.24
90	16.8	2.30	4.34
100	16.3	2.23	4.48
120	15.5	2.12	4.71
140	14.8	2.02	4.94
160	14.1	1.93	5.18
180	13.5	1.85	5.40
240	12.0	1.64	6.09

Initial concentration of acetone and DNPH: 3.0×10^{-3} M; ionic strength of the reaction medium: 4.2×10^{-1} M; temperature: 25°C