

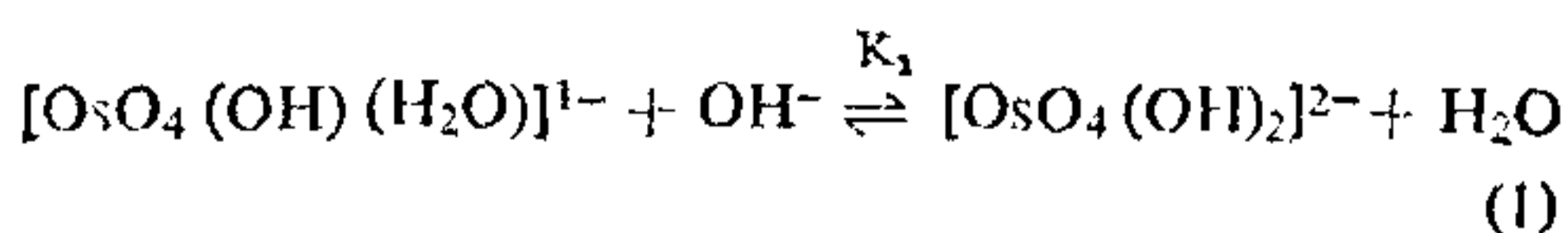
**KINETICS OF Os (VIII) CATALYSED
OXIDATION OF CYCLOHEXANOL
BY PERIODATE**

OSMIUM TETROXIDE is known to act as an effective catalyst in the oxidation of many organic compounds by oxidants like alkaline ferricyanide¹ chloramine-T², periodate³⁻⁵ etc. Though simple alcohols were not affected, benzyl and substituted benzyl alcohols⁵ were reported to be oxidized by periodate both in the presence and absence of OsO₄. Cyclohexanol does not react with periodate under normal conditions. It is therefore thought worthwhile to find out whether OsO₄ acts as a catalyst in the oxidation of cyclohexanol by periodate and if so to find out the mechanism.

All the chemicals used were of Analar grade and cyclohexanol was freshly distilled before use. Known volumes of cyclohexanol was directly added to the reaction flask containing required quantities of periodate, OsO₄ and NaOH, after thermostating the latter for one half hour. Unreacted periodate was estimated iodometrically each time using phosphate buffer (pH ≈ 5-5.5). Adipic acid was found to be the final product as checked by its m.p. (148°C). Reaction mixture containing [periodate] ≫ [cyclohexanol] in the presence of [OsO₄] = 7.60 × 10⁶ M and [NaOH] = 0.03 M was kept for two days at room temperature and the unreacted periodate was estimated. Four moles of periodate were found to react with one mole of cyclohexanol.

The rate of the reaction was found to be independent of the initial [periodate], exhibiting zero order kinetics (Table I). The order in [cyclohexanol] and [OsO₄] were found to be one each as can be seen from the data in Table I. The k₀ values (where k₀ is zero order rate constant) increased with increase in [OH⁻] and reached a constant value at high [OH⁻]. The plot of log k₀ vs log [OH⁻] was linear (Fig. 1) in the concentration region 0.017 M-0.068 M with a slope of 0.55. Similar type of behaviour was also observed in the oxidation of alcohols by chloramine-T², but with negative fractional order in [OH⁻]. The effect of added salts, viz., NaCl and NaClO₄ on the rate was found to be negligible.

OsO₄ is known to exist as [OsO₄ (OH) (H₂O)]¹⁻ and [OsO₄ (OH)₂]²⁻ in alkaline medium^{6,7a,b}. The existence of these species might be considered according to the following equilibrium.



Since the rate of oxidation was found to increase with increase of [OH⁻], the complex [OsO₄(OH)₂]²⁻ may be expected to be the reactive species. It is well known that the transition metal complexes are good hydride ion abstracting agents both in alkaline^{8a,b} and acid⁹

TABLE I

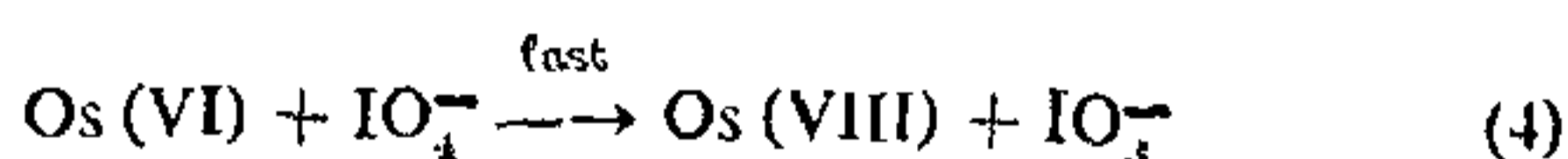
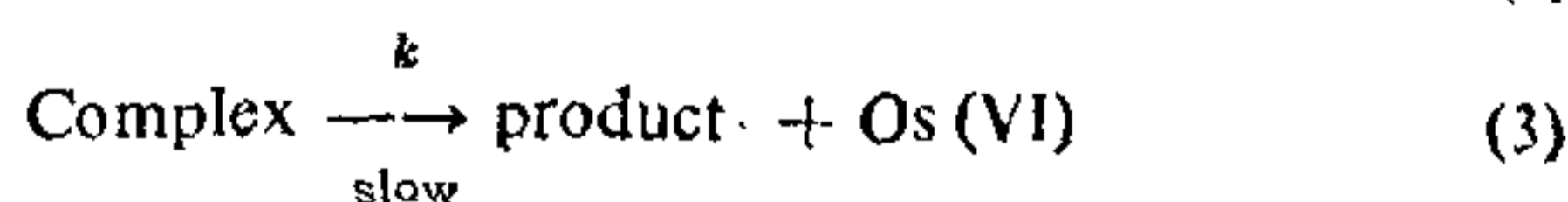
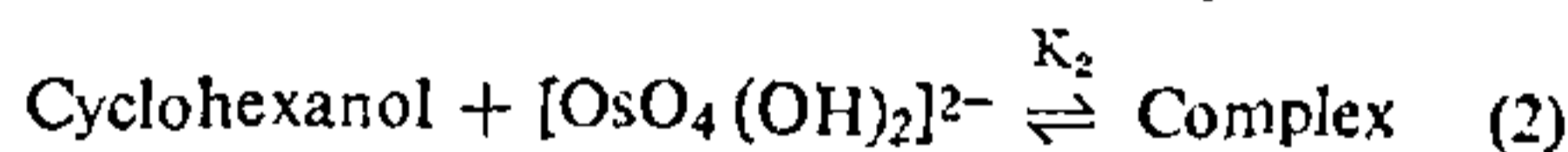
Dependence of rate constant on [oxidant], [cyclohexanol] and [OsO₄]

[NaOH] = 0.034 M

T = 308°K

[periodate] × 10 ⁴ mol. lit ⁻¹	[cyclohexanol] × 10 ² mol. lit ⁻¹	[OsO ₄] × 10 ⁶ mol. lit ⁻¹	k ₀ × 10 ⁵ mol. lit ⁻¹ min ⁻¹	k ₀ × 10 ³ mol. lit ⁻¹ min ⁻¹	k ₀ × 10 mol. lit ⁻¹ min ⁻¹
4.00	2.00	7.60	2.11
8.00	2.00	7.60	2.17
10.0	2.00	7.60	2.18
20.0	2.00	7.60	2.18
40.0	2.00	7.60	2.18
20.0	1.00	7.60	1.10	1.10	..
20.0	4.00	7.60	4.22	1.06	..
20.0	6.00	7.60	5.81	0.968	..
20.0	8.00	7.60	8.17	1.02	..
20.0	2.00	1.90	0.496	..	0.261
20.0	2.00	3.80	1.03	..	0.271
20.0	2.00	15.2	3.72	..	0.245
20.0	2.00	19.0	5.15	..	0.271

solutions. In view of the above facts a probable mechanism involving the formation of the complex between [OsO₄(OH)₂]²⁻ and cyclohexanol, which latter decomposes to the products is proposed.



On the basis of the equations 1, 2 and 3 the rate expression for the disappearance of [IO₄⁻] comes out to be

$$\frac{-d[\text{IO}_4^-]}{dt} = k_0 = \frac{k K_1 K_2 [\text{cyclohexanol}] [\text{Os (VIII)}] [\text{OH}^-]}{1 + K_1 [\text{OH}^-]} \quad (5)$$

which substantiates the rate data obtained. At high [OH⁻], equation (5) reduces to

$$\frac{-d[\text{IO}_4^-]}{dt} = k K_2 [\text{cyclohexanol}] [\text{Os (VIII)}] \quad (6)$$

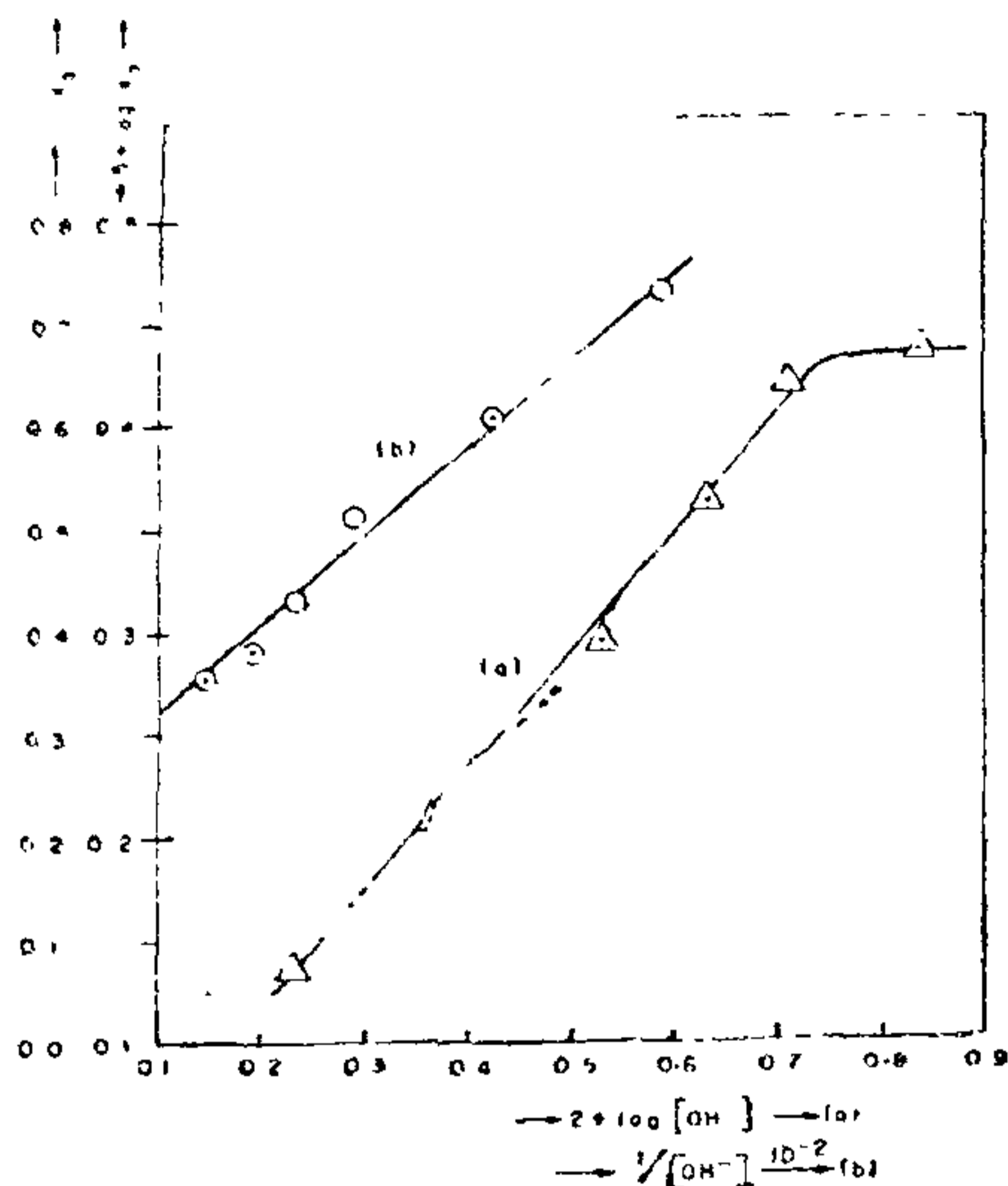


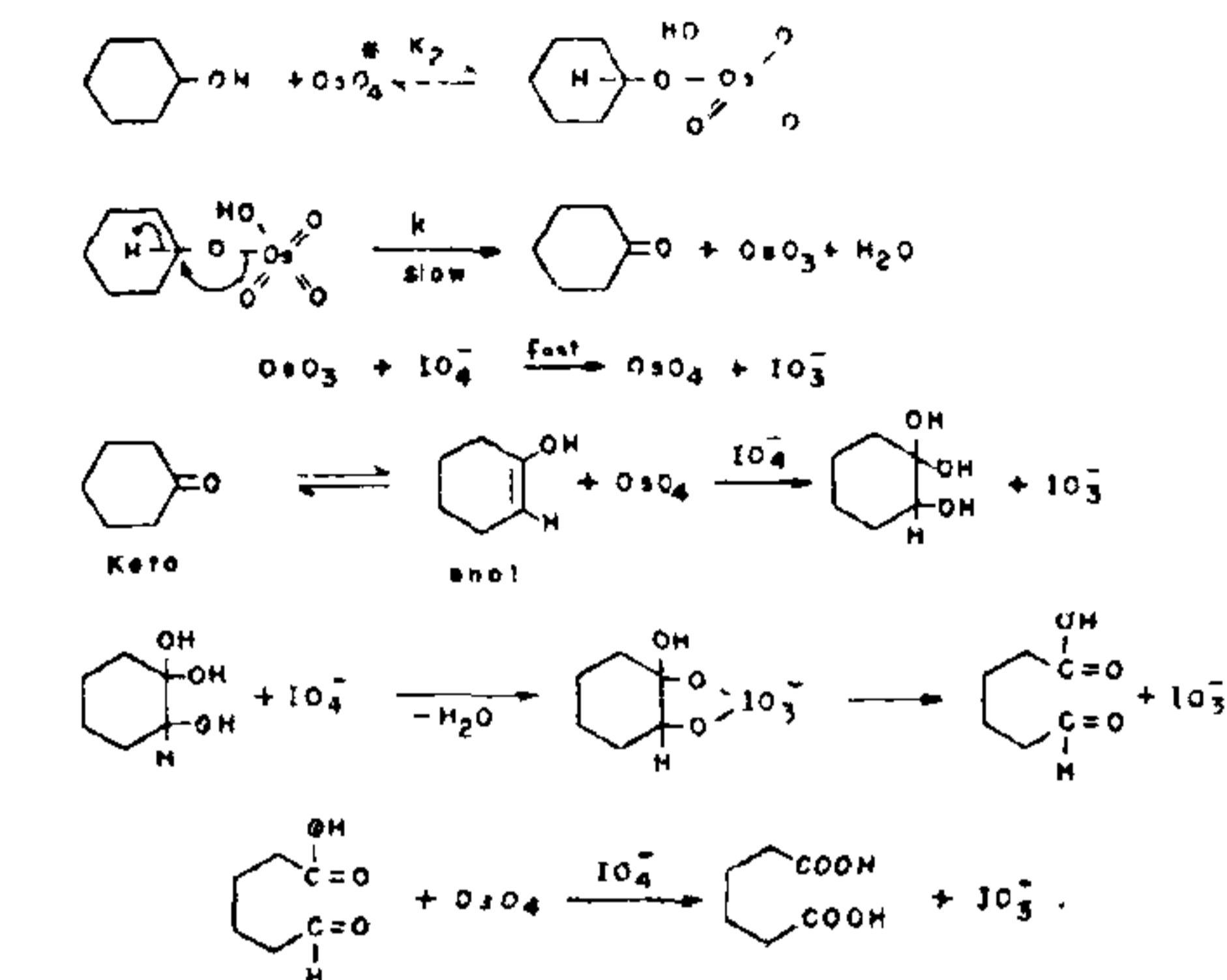
FIG. 1. (a) Plot of $\log k_0$ vs $\log [\text{OH}^-]$, (b) plot of $1/k_0$ vs $1/[\text{OH}^-] \times 10^{-2}$ [periodate] = 2.00×10^{-3} M; [cyclohexanol] = 2.00×10^{-2} M; $[\text{OsO}_4] = 7.60 \times 10^{-6}$ M; $T = 313^\circ \text{K}$.

which is in accordance with the results obtained (Fig. 1). Such type of behaviour was also observed in the oxidation of alcohols by alkaline ferricyanide¹ in the presence of Os(VIII). By taking reciprocals of equation (5) we get

$$\frac{1}{k_0} = \frac{1}{k K_1 K_2 [\text{cyclohexanol}] [\text{Os(VIII)}] [\text{OH}^-]} + \frac{1}{k K_2 [\text{cyclohexanol}] [\text{Os(VIII)}]} \quad (7)$$

A plot of $1/k_0$ vs $1/[\text{OH}^-]$ was linear with a positive slope and intercept (Fig. 1) supporting the proposed mechanism. The various steps proposed for cyclohexanol are given in Chart I.

The intermediate product cyclohexanone in its enol form can be hydroxylated by OsO_4 (due to $\text{C}=\text{C}$)₁ to give 1, 2-diol type of a compound which is oxidised rapidly by periodate. The initial rates of oxidation of cyclohexanol (2.00×10^{-2} M) and cyclohexanone (0.50×10^{-3} M) under similar conditions ($[\text{IO}_4^-] = 2.00 \times 10^{-3}$ M, $[\text{NaOH}] = 0.034$ M, $[\text{OsO}_4] = 7.60 \times 10^{-6}$ M, $T = 313^\circ \text{K}$) were found to be 2.79×10^{-5} and 11.0×10^{-5} mol lit⁻¹ sec⁻¹ respectively. This clearly shows that cyclohexanone gets oxidised rapidly to a 1, 2-diol type of intermediate. This is further cleaved by periodate which is a specific oxidant for



* $[\text{OsO}_4(\text{OH})_2]^{2-}$ is written as OsO_4 for simplicity

CHART I

1, 2-glycols giving the final product, viz., adipic acid. The activation parameters were found to be as follows:

$$E_{\text{exp}} = 13.8 \text{ K cal mol}^{-1}, \quad \Delta S^\ddagger = -37.7 \text{ cal deg}^{-1} \text{ mol}^{-1}.$$

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July 12, 1978.

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- Singh, H. S., Singh, S. P., Singh, S. M., Singh, R. K. and Sisodia, A. K., *J. Phys. Chem.*, 1975, 79, 1920.
- Radhakrishnamurti, P. S. and Sahu, B., *Indian J. Chem.*, 1978, 16 A, 259.
- Subas, C. Pati, Sriramulu, Y., *Ibid.*, 1978, 16 A, 74.
- Panigrahi, G. P. and Prafulla Misrao, K., *Ibid.*, 1978, 16 A, 201.
- Subas, C. Pati and Sriramulu, Y., *Annual Convention of Chemists (Abstracts)*, 1977, Org. p. 71.
- Mayell, J. S., *Ind. Engng. Chem.*, 1968, 7, 12.
- (a) Griffith, W. P., *Q. Rev.*, 1965, 19, 254.
(b) Cotton, F. A. and Wilkinson, G., *Advanced Inorganic Chemistry*, Wiley Eastern, New Delhi, 1966, p. 1007.
- (a) Chatt, J. and Shaw, B. L., *Chem. Ind.*, 1961, p. 290.
(b) Singh, H. S., Singh, R. K., Singh, S. M. and Sisodia, A. K., *J. Phys. Chem.*, 1977, 81, 1044.
- Charman, H. B., *J. Chem. Soc. (B)*, 1967, p. 629.
- Buist, G. J., Buntin, C. A. and Miles, J. H., *Ibid.*, 1957, p. 4567.