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Heats of Formation & Lattice Energies of α-, β- & γ-Picoline Complexes of Copper Fluoborate

A. Chatterjee & G. C. Bhattacharya

Department of Chemistry, St Xavier's College, Ranchi

and

Chemistry Department, Ranchi University, Ranchi

Received 11 *December* 1975; *accepted* 28 *June* 1976

Kapustiniskii's equation and a thermochemical cycle have been employed for the determination of lattice energy of α-, β- and γ-picoline complexes of copper fluoborate. The divergent results obtained for a particular complex by the two methods do not permit an assessment of stability order of comparable complexes.

HEATS of formation and lattice energies of β- and γ-picoline complexes of Co, Zn and Cd fluoborate have been already reported by Bhattacharya and Dasgupta[1]. In this note heats of formation and lattice energies of α-, β- and γ-picoline complexes of copper fluoborate have been determined. In each case three readings were taken and the mean has been reported. Heats of formation (Q) determined by applying[1] Hess's law of heat summation are 197·83, 230·85 and 237·97 kJ mole⁻¹ for Cu(BF₄)₂4α-Pic, Cu(BF₄)₂4β-Pic and Cu(BF₄)₂4γ-Pic respectively.

Calculation of lattice energy — Of the available equations[2] for the calculation of lattice energy that of Kapustiniskii[3] was found simple. In a second attempt, use was made of a thermochemical cycle[4].

The expression: $U_2 = U_1 + Q - E$ where U_2 = lattice energy of complex salt, U_1 = lattice energy of simple salt, Q = heat of formation of the complex salt and E = coordination energy. U_1 is evaluated from Kapustiniskii's equation, Q is experimentally determined and E is theoretically calculated from the equation of Yatsimirskii[5]. The values thus found from Kapustiniskii's equation and from thermochemical cycle consideration are given in Table 1.

The data in Table 1 show that the application of lattice energy to assess the stability order of comparable complexes may not be helpful, since the values of U_2 obtained using Kapustiniskii's equation and thermochemical cycle differ widely even for the same complex. Similar divergent values have been reported by Bhattacharya and Dasgupta[1] in their work on β- and γ-picoline complexes of Co, Ni and Zn fluoborates. This large discrepancy in values has been reported[6] for the compounds like [Fe(NH₃)₆]Cl₂ and [Mn(NH₃)₆]Cl₂.

According to Kapustiniskii's equation, the lattice energies of the three systems 4, 3 and 2 of a particular compound decrease in this order, whereas reverse is true when lattice energies are obtained by the application of thermochemical cycle. The heat of formation cannot be found out with any fair degree of accuracy and hence there is uncertainty in the evaluation of lattice energy by thermochemical methods. Keeping in view the results of the present and previous work, it may be inferred that the determination of the lattice energies with present forms of equations cannot be helpful to assess the stability of the complex compounds.

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Polymerization of Methyl Methacrylate by Ammonium Hexachlororhodate(III)

M. M. Taqui Khan & Q. Anwaruddin

Departments of Chemistry, Indian Institute of Technology Madras 600036 and Nizam College, Hyderabad 500001

Received 9 *February* 1976; *accepted* 29 *May* 1976

The kinetics of Rh(III)-catalysed polymerization of methyl methacrylate were studied under strictly deaerated conditions at 60°±0·1°C. The rate of polymerization was measured by a gravimetric determination of the monomer disappearance. Monomer and catalyst concentrations were varied, and the rate of polymerization was found to be proportional to [monomer]²·⁵ and [catalyst]⁰·³⁵. The chain lengths of the various PMMA samples obtained in the experiments were determined by a measurement of their viscosities in benzene solutions. In the light of the experimental results, a tentative initiation step for polymerization was proposed.

RHODIUM salts have been recently used as catalysts in the polymerization of butadiene[1,2] and methyl acrylate[3]. In the Rh³⁺-catalysed polymerization of butadiene, the polymer had a high steric purity and any chance of random free radical type of polymerization was inhibited by Rh³⁺. The conditions for the polymerization of butadiene, however, varied vastly from one rhodium

TABLE 1 — LATTICE ENERGY OF THE COMPLEX SALTS

Compound	U_2 (kJ/mole)	
	Kapustiniskii	Thermochemical cycle
Cu(BF₄)₂4α-Pic	1093·97	1280·79
Cu(BF₄)₂3α-Pic	1017·95	1303·81
Cu(BF₄)₂2α-Pic	935·50	1332·65
Cu(BF₄)₂4β-Pic	1093·97	1276·31
Cu(BF₄)₂3β-Pic	1017·95	1305·03
Cu(BF₄)₂2β-Pic	935·50	1318·26
Cu(BF₄)₂4γ-Pic	1093·97	1272·75
Cu(BF₄)₂3γ-Pic	1017·95	1312·90
Cu(BF₄)₂2γ-Pic	935·50	—

catalyst to other. The use of an emulsifier, like sodium dodecylbenzene sulphonate in such systems enhanced considerably the rate of polymerization by a mechanism which is not very well understood.

Dimerization of methyl acrylate was achieved[3] at 140° by the use of $RhCl_3.3H_2O$ as catalyst and the yield of dimer was found to increase by the addition of ethylene to the reaction system. As kinetic work on Rh(III)-catalysed vinyl polymerization has not been attempted so far, the present investigation was carried out with the aim of studying the kinetics of the polymerization of methyl methacrylate using ammonium hexachlororhodate(III) as the catalyst.

Reagents — All the chemicals used were of BDH (Analar), E. Merck (GR) or MB reagent grade. Water triply distilled over alkaline permanganate was used for the preparation of solutions. Absolute ethyl alcohol was redistilled before use. The monomer methyl methacrylate (Rohm & Haas Co., USA) was washed free of inhibitor with a solution of sodium hydroxide (5%), then with water, and finally distilled under reduced pressure under N_2 atmosphere.

The system consisting of ammonium hexachlororhodate(III)-ethanol-water was deaerated by passing oxygen-free nitrogen (the oxygen being removed by bubbling the nitrogen through VSO_4 solution) through the solution for about 30 min. Methyl methacrylate was then added and the deaeration continued for a further period of 15 min. The reaction tube was then placed inside a thermostat maintained at $60° \pm 0.1°C$ and the reaction allowed to proceed for 1 hr. The polymer obtained as a precipitate was filtered through a sintered glass crucible, dried and weighed. The rate of monomer disappearance $(-d[M]/dt)$ was then calculated from the weight of polymer obtained.

The viscosities of solutions of the PMMA (0·1%) in benzene were measured in a viscometer thermostated to $25° \pm 0.1°$ in a viscometric-bath designed for precision viscometry (Krebs Electrical & Manufacturing Co., New York). Viscosity measurements were used for the evaluation of chain lengths with the help of Eq. (1)[4]

$$n = 2.81 \times 10^3 [\eta]^{1.32} \qquad \qquad ...(1)$$

where n is chain length and $[\eta]$ is intrinsic viscosity.

In pure aqueous solution (in the absence of alcohol) no polymerization of methyl methacrylate could be detected. This may be due to the limited solubility of methyl mathacrylate in water (about 1·4 ml in 100 ml of water). Ethanol being a good solvent for methyl methacrylate was therefore used and it did not initiate thermal polymerization by itself. A pure ethanol medium also could not be used, as the catalyst was insoluble in it. Hence, a water-alcohol mixture containing alcohol as the major component was used. The rate of polymerization, $-d[M]/dt$, was found to decrease with increase in time (Table 1) and the rate of reaction, $-d[M]/dt$, was found to be proportional to [monomer]$^{2.5}$ (Fig. 1). The order with respect to the [monomer] viz. 2·5, was greater than 1 and this may be explained by considering the monomer to form a probable complex with the

TABLE 1 — DEPENDENCE OF RATE OF POLYMERIZATION OF MMA ON TIME

{[Monomer]: 1·253 moles litre^{-1}; [Catalyst]=1.10^{-3} moles litre^{-1}; temp.=60°C}

Reaction period (hr)	$-d[M]/dt$ $\times 10^6$ litre^{-1} sec^{-1}	Reaction period (hr)	$-d[M]/dt$ $\times 10^6$ moles litre^{-1} sec^{-1}
$\frac{1}{2}$	9·63	3	2·49
1	8·15	4	3·83
$1\frac{1}{2}$	4·91	6	2·83

hexachlororhodate(III) anion which then generated free radicals by a redox reaction taking place intramolecularly for initiation of polymerization[5].

The free radical nature of the Rh(III)-catalysed polymerization of methyl methacrylate was further evidenced by the usual free radical retarders, oxygen and *m*-dinitrobenzene, lowering the rates of the polymerization reaction as compared to the rate in the deaerated system. The following rates were observed under different conditions:

Reaction condition	*Rate*
Undeaerated (i.e. in the presence of atmospheric oxygen)	0.7406×10^{-6} mole litre^{-1} sec
In the presence of *m*-dinitrobenzene (conc.: 10·67 mmoles)	1.592×10^{-6} mole litre^{-1} sec^{-1}
Deaerated (i.e. in the absence of atmospheric oxygen)	9.387×10^{-6} mole litre^{-1} sec^{-1}

The rate of reaction, $-d[M]/dt$, was also found to be proportional to [catalyst]$^{-0.35}$ (Fig. 2), indicating that the catalyst effectively terminated the chain reaction. The rate of the reactions decreased with an increase in the concentration of the catalyst. This is expected for Rh^{3+} which is a good inhibitor[6] of free radical polymerization. As the water content of the water-ethanol reaction medium was increased
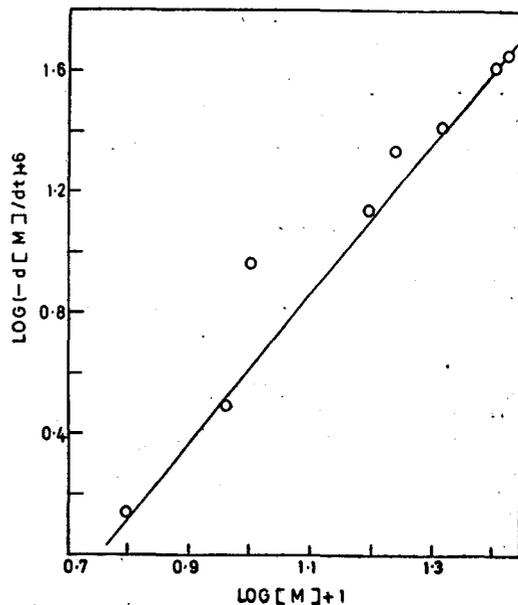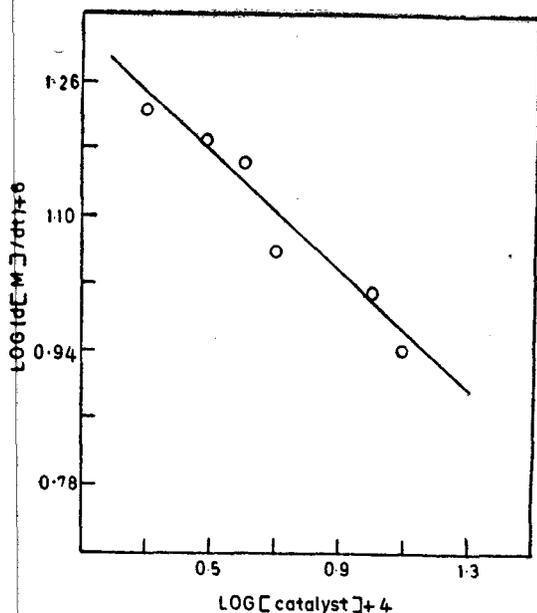

Fig. 1 — Plot of log $(-d[M]/dt)$ versus log [monomer]

Fig. 2 — Plot of log $(-d[M]/dt)$ versus log [catalyst]

TABLE 2 — EFFECT OF VARYING WATER CONTENT OF THE REACTION MEDIUM ON THE RATE OF Rh^{3+}-CATALYSED POLYMERIZATION OF MMA

{[Monomer]$=2$ ml (1.253 mole litre^{-1}); time of reaction$=1$ hr; [Catalyst]$=1.5$ ml of 1×10^{-2} mole litre^{-1}; solution (1×10^{-3} mole litre^{-1}); temp.$=60°$; total vol$=15$ ml}

Water ml	Ethanol ml	$-d[M]/dt \times 10^5$ (moles litre^{-1} sec^{-1})	log $-d[M]/dt+6$	Chain length n
0.5	11.0	0.47	0.6721	—
1.0	10.5	1.39	1.1431	1081
1.5	10.0	1.36	1.1335	1096
2.0	9.5	1.88	1.2967	1273
2.5	9.0	2.09	1.3201	2458
3.0	8.5	2.39	1.3784	1909
3.5	8.0	2.22	1.3464	1445
4.0	7.5	1.99	1.2989	2186
5.0	6.5	1.51	1.1790	1808
6.0	5.5	1.66	1.2201	2094

a gradual increase in the rate was observed up to a composition of 33.3% water (maximum rate) after which the rate dropped down gradually (Table 2). Chain lengths of the PMMA samples increased with an increase in the monomer concentration and decreased with the catalyst concentration, in the manner expected from the rate equation.

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Kinetics of Ag(I) Catalysed Oxidation of Isoamyl Alcohol by Peroxydisulphate

R. N. SINGH, L. N. SINGH & H. S. SINGH

Department of Chemistry, University of Allahabad, Allahabad

Kinetics of Ag(I)-ion catalysed oxidation of isoamyl alcohol by peroxydisulphate has been studied in aqueous medium. The reaction shows first order kinetics with respect to peroxydisulphate and zero order with respect to isoamyl alcohol. The effect of varying [Ag$^+$] on the reaction rate indicates the direct proportionality on [Ag$^+$] even at different temperatures. A probable mechanism has been suggested.

THE kinetics of oxidation of isoamyl alcohol has been studied by a number of workers using oxidants such as potassium permanganate[1], potassium dichromate[2], cobalt bromide[3], nitric acid[4], *tert*-butyl chromate[5] and chromic acid[6]. The present note deals with the results of kinetics of silver(I)-ion catalysed oxidation of isoamyl alcohol by peroxydisulphate in aqueous medium.

All the chemicals (Analar or GR) were procured from either BDH or E. Merck.

The progress of reaction was followed by estimating unreacted $K_2S_2O_8$ iodometrically[7] at various intervals of time in pyrex glass bottle, coated on the outside with black Japan and wrapped with black cloth.

The results given in Table 1 indicate the first order kinetics with respect to peroxydisulphate. The overall first order velocity constant (k_a), velocity constant (k_d) for the decomposition of the peroxydisulphate and first order velocity constant (k) for the oxidation of isoamyl alcohol at different [peroxydisulphate] are also given in Table 1. The order of reaction with respect to isoamyl alcohol has been found to be zero (Table 2). A perusal of Fig. 1 clearly demonstrates the direct proportionality of the reaction rate on [Ag$^+$] even at different temperatures.

TABLE 1 — EFFECT OF VARYING [$S_2O_8^{2-}$] ON THE REACTION RATE

{[Isoamyl alcohol]$=2.87\times10^{2-}M$; [Ag$^+$]$=1.0\times10^{-3}M$; temp.$=55°$}

[$S_2O_8^{2-}$]$\times10^2 M$	0.5	1.0	1.5	2.0	2.5
$k_a\times10^3$ min^{-1}	27.10	26.26	26.10	25.80	25.21
$k_d\times10^3$ min^{-1}	6.07	5.81	5.34	4.66	4.50
$k\times10^3$ min^{-1}	21.03	20.45	20.76	21.14	20.71

TABLE 2 — EFFECT OF VARYING [ISOAMYL ALCOHOL] ON THE REACTION RATE

{[$S_2O_8^{2-}$]$=1.0\times10^{-2}M$; [Ag$^+$]$=1.0\times10^{-3}M$; temp.$=55°$}

(Isoamyl alcohol)$\times10^2 M$	1.435	2.870	4.305	5.740
$k_a\times10^3$ min^{-1}	27.03	26.26	26.77	26.85
$k_d\times10^3$ min^{-1}	5.81	5.81	5.81	5.81
$k\times10^3$ min^{-1}	21.22	20.45	20.96	21.04