

Resin-Supported Vanadium (IV)-Catalysed Epoxidation of Maleic, Fumaric, and Crotonic Acids with Hydrogen Peroxide

In recent years polymer-supported transition metal catalysts have been successfully employed for the epoxidation of various α,β -unsaturated acids (1), cyclohexene (2, 3), and styrene (4). The main advantage of using polymer-supported catalysts is their easy separation from the reaction mixture and higher catalytic activity along with greater stability (1, 2).

This paper deals with the synthesis of polymer-supported vanadium catalysts and kinetic studies on epoxidation of maleic acid, fumaric acid, and crotonic acid.


All the chemicals used were of A.R. Grade. $[\text{VO}(\text{acac})_2]$ complex was prepared according to the literature method (5) and was supported on nonporous Amberlite IR-120 (16-45 mesh) of spherical beads. The polymer-supported $[\text{VO}(\text{acac})_2]$ complex was prepared by a method similar to one reported by Bhaduri *et al.* (2). Anchored catalyst contained 3.6 mg vanadium/g beads.

It was observed that an increase of pH up to 10 or of temperature up to 60°C dissociated the resin-bound catalyst by around 45%. Nonetheless, the resin-bound catalyst was found to be quite stable up to pH 5 and at a temperature of 40°C. The infrared spectrum peak at 1580 cm^{-1} of anchored beads was found unaltered before and after epoxidation reactions.

Epoxidation reactions were carried out under nitrogen atmosphere by adjusting the pH of the reaction mixture with triethanolamine. Variation in stirring rate per minute from 700 to 2000 did not effect the reaction rate and hence showed no effect of external mass transfer. Subsequently all kinetic ex-

periments were carried out at a stirring rate of ~ 1000 rpm with a magnetic stirrer. Hydrogen peroxide was estimated colorometrically (6).

The presence of epoxide formed in the reaction was confirmed by a method given by Jungnickel *et al.* (7). The progress of the reaction was monitored by tlc using benzene : ethanol (5 : 1, v/v) solvent till only one spot on tlc plate corresponding to epoxide remained. Spots of substrate and epoxide on tlc plates were detected by exposing plates to iodine fumes. Epoxides were extracted with solvent ether. Infrared spectra of the epoxides were recorded on a Perkin-Elmer-399 IR spectrophotometer, which gave peaks 1235-1250 cm^{-1} (symmetrical stretching), 845-860 cm^{-1} (C-H

stretching), and 2970-2985 cm^{-1} ( ring).

It was observed that hydrogen peroxide decomposition remains negligible up to pH 5, above which decomposition increases rapidly. Similar observations were made by Beg and Ahmad (8). The amount of hydrogen peroxide disappearance due to decomposition was adjusted against the actual amount consumed in epoxidation by running a blank with every reaction set.

Epoxidation reactions were carried out under pseudo-first-order conditions. A plot of $\log[\text{H}_2\text{O}_2]$ vs time gave a straight line showing the order with respect to the oxidant as one. Further, a plot of $\log k_{\text{obs}}$ vs $\log[\text{substrate}]$ gave a straight line with a slope of unity showing the order with respect to substrate also as one. Values of k_{obs}

TABLE 1
Effect of Concentration of Substrate on the Rate of Epoxidation

Substrate	Substrate concentration (<i>M</i>)	$k_{\text{obs}} \times 10^2$ (min^{-1})	$k_{\text{obs}} \times 10^2/[\text{Subs}]$ ($\text{mol}^{-1} \text{min}^{-1}$)
Fumaric acid	0.120	0.93	7.75
	0.133	1.05	7.89
	0.144	1.22	8.21
	0.166	1.35	8.13
	0.177	1.46	8.22
Maleic acid	0.120	0.81	6.60
	0.133	0.91	6.80
	0.144	1.06	7.31
	0.166	1.17	7.04
	0.177	1.24	7.01
Crotonic acid	0.120	1.10	7.84
	0.133	1.25	8.21
	0.144	1.30	8.29
	0.166	1.72	8.74
	0.177	1.92	8.51

Note. $[\text{H}_2\text{O}_2] = 0.013 \text{ M}$; pH 4.5; $[\text{Catalyst}] = 3.4 \times 10^{-4} \text{ M}$; $[\text{Temp}] = 32 \pm 1^\circ\text{C}$.

when divided by corresponding concentration of acids gave a constant value, further confirming the order of the reaction with respect to the substrate as one (Table 1).

The rate of epoxidation of acids increased with pH and was found to be a maximum at pH 5. A decrease in epoxidation rate above pH 5 (Table 2) is conceivable due to rapid

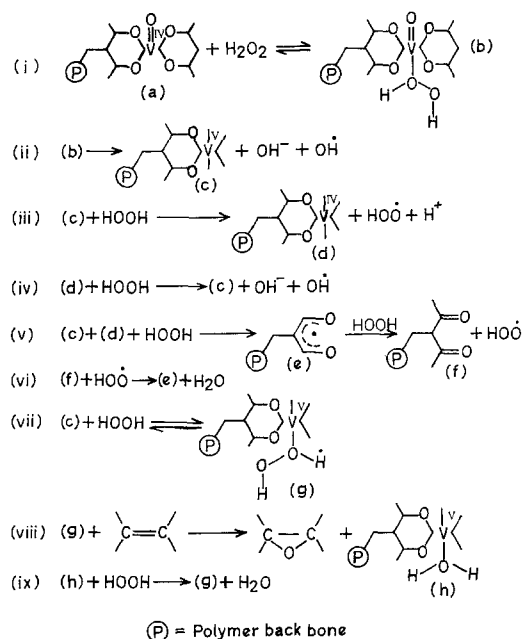
decomposition of H_2O_2 at higher pH. Further, the stability of the polymer-supported catalyst is also low at higher pH.

To compare the activity of resin-supported complex with that of unsupported, two sets were simultaneously run keeping other parameters constant. It was observed that the reaction involving resin-supported

TABLE 2
Effect of pH on the Rate of Epoxidation of Maleic, Fumaric, and Crotonic Acid

pH values	$k_{\text{obs}} \times 10^2$ fumaric acid	$k_{\text{obs}} \times 10^2$ maleic acid	$k_{\text{obs}} \times 10^2$ crotonic acid
3.0	1.64	1.53	1.76
3.5	1.71	1.52	1.90
4.0	1.81	1.70	2.72
4.5	1.78	1.66	2.19
5.0	1.61	1.49	2.11
6.0	1.51	1.31	1.64
9.0	1.21	1.10	1.46

Note. $[\text{Catalyst}] = 3.10 \times 10^{-4} \text{ M}$; $[\text{Substrate}] = 0.12 \text{ M}$; $[\text{Temp}] = 35 \pm 1^\circ\text{C}$; $[\text{H}_2\text{O}_2] = 0.013 \text{ M}$.



SCHEME 1. Tentative sequence of epoxidation reaction.

catalyst is faster nearly by a factor of two than the reaction using unsupported vanadium catalyst.

Extensive work has been conducted on catalytic oxidation of organic compounds with hydroperoxides in the presence of [VO(acac)₂] as a catalyst (9–11). On the basis of results, a tentative sequence of reactions can be described in the following manner (see Scheme 1). The catalyst is first activated through a rapid irreversible step via a red intermediate (b), taken as a vanadium(IV) hydroperoxide complex to a vanadium(V) species (c). The reaction produces hydroxy radicals which can initiate a competing radical-chain decomposition process (d), (e), and (f). Reversible formation of a complex between the vanadium species and hydrogen peroxide then takes place. The subsequent rate-determining oxygen

atom transfer from this complex to the organic reactant gives the final oxidised product and water.

From Table 1 it is evident that the presence of an electron-donating methyl group in crotonic acid enhances the rate of epoxidation. Further, the epoxidation rate of fumaric acid is greater than that of maleic acid. The electron density on the double bonds for both the acids is the same but probably the formation of the intermediate complex is difficult in the case of maleic acid as both the carboxylic groups are at *cis* position. The values of activation energy determined as 19.70, 18.40, and 5.57 kJ mol⁻¹ for maleic, fumaric, and crotonic acids, respectively, support the above observations.

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