Polymerization of Acrylamide Initiated by Quinquevalent Vanadium–Cyclohexanone Redox System

Rajani K. Samal, Padma L. Nayak,* and Trijama R. Mohanty

Department of Polymer Chemistry, Ravenshaw College, Cuttack-3 (Orissa), India. *Received March 17, 1976*

ABSTRACT: The polymerization of acrylamide initiated by the quinquevalent vanadium–cyclohexanone redox pair has been investigated in aqueous media in nitrogen atmosphere. The rate of polymerization is proportional to the square of the monomer concentration and first power of cyclohexanone concentrations, and the reciprocal of the rate of polymerization is proportional to the first power of [V(V)]. The rate of vanadium ion disappearance, $-R_v$, is proportional to [CH] and [V(V)]. The effect of certain salts and organic solvents on the rate of polymerization has been investigated. A suitable kinetic scheme has been proposed and the values of k_p/k_t and k_0/k_i were reported.

The aqueous polymerization of acrylamide initiated by metal ion organic substrate redox system is unique since polyacrylamide is soluble in water and the system is no longer heterogeneous as has been observed in the case of the polymerization of acrylonitrile, methyl acrylate, methyl methacrylate, and other heterophase systems. The various rate equations which have certain limitations for the heterogeneous systems can smoothly be applied for homogeneous systems without any difficulty. The aqueous polymerization of acrylamide has been reported with several redox systems like permanganate–organic substrate,[1–3] cerium(IV)–organic substrate,[4–9] and chromium(VI)–organic[10] substrate redox systems. In the present investigation, we wish to report the aqueous polymerization of acrylamide by the quinquevalent vanadium–cyclohexanone redox system in sulfuric acid medium. The various rate data have been evaluated and a plausible mechanism has been suggested.

Experimental Section

Acrylamide was recrystallized from methanol and then dried in vacuo over silica gel, melting point 84.5 °C. Ammonium metavanadate (AR), sodium bisulfate (Riedel), and sulfuric acid (~18 M; AR Basynth, India) were used. Cyclohexanone (CH) was purified by two fractional distillations through a 7 in. vigreux column under an atmosphere of nitrogen. Middle fractions (bp 156 °C) were collected and stored over Linde molecular sieves. Water, distilled three times over alkaline permanganate and deionized by passing through a column of Bioderminrolit resin (Permutit Co., U.K.), was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing it through several columns of Fieser's solution, a column of saturated lead acetate solution, and finally a wash bottle containing distilled water.

Preparation of V(V) stock solutions, their estimations, etc., have already been described in our previous communications.[11,12] The polymer was separated by pouring the reaction mixture into methanol, filtering the polymer, and drying at room temperature under reduced pressure. Rates of polymerization were obtained gravimetrically, while rates of oxidant consumption were obtained by vanadometry on reaction mixtures arrested by addition of excess standard ferrous sulfate solution. Polymer samples were dissolved in dimethylformamide and reprecipitated in cold methanol.

Discussion

Rate Dependence on Activator Concentration. The percentage conversion data at varying concentrations of cyclohexanone (activator) and at fixed concentrations of quinquevalent vanadium (catalyst), H_2SO_4, and monomer are shown in Figure 1. The initial rate of polymerization as well as the percentage of conversion increases with an increase of activator concentration (0.2–0.4 M). This may be attributed to the fact that the increasing quantity of cyclohexanone (CH) produces an increased quantity of free radicals, whereby the maximum conversion is increased.

The rate of polymerization increased linearly with an increase in cyclohexanone concentration. Linear plots of log R_p vs. log [CH] with unit slopes as well as R_p vs. [CH] plots with zero intercepts (Figure 4) indicated that the order with respect to [CH] was unity. The most interesting observation is that the values of R_p increase linearly with an increase of [CH] up to 0.4 M and then fall gradually and level off.[13] This might be due to the transfer of radical with cyclohexanone.

Rate Dependence on the Catalyst Concentration. The percentage of conversion data at varying concentrations of the catalyst and fixed concentration of the activator and monomer is shown in Figure 3. At low concentration of the catalyst, [V(V)], the initial rate of polymerization as well as the percentage of conversion increases (0.01–0.03 M), but at a higher concentration of the catalyst the percentage of conversion decreases considerably ([V(V)] = 0.04 and 0.06 M). Such observation can be explained by considering the termination mechanism. Linear termination of vinyl polymerization by metal ions is now well recognized,[14,15] so when the concentration of V(V) becomes very high, the termination of the polymer chain takes place more preferentially and hence the percentage of polymerization decreases. The other alternative is that by increasing the concentration of the catalyst the primary radicals are produced at a faster rate so that termination is due partly to these radicals and hence the percentage of polymerization decreases. A similar explanation has also been furnished by Misra and co-workers[1–3] and by Palit and co-workers[16,18] in the case of permanganate–oxalic acid catalyst polymerization of vinyl monomers.

The rate of polymerization was inversely proportional to [V(V)], $1/R_p$ [V(V)] plots being linear with intercept on the ordinate (Figure 7). An increase in [V(V)] (0.02–0.08 M) increased the rate, and a first-order dependence of the rate on [V(V)] was concluded from the linear plots of $-R_v$ vs. [V(V)]. An increase in [CH] increases $-R_v$; at high [CH], plots of $-R_v$ vs. [CH] were curved (Figure 5). Similar observations were noted by us in the polymerization of acrylonitrile initiated by the V(V) + cyclohexanone redox system.[11]

Rate Dependence upon Monomer Concentration. A regular increase in rate (R_p) was noticed with an increase in monomer concentration [M] (0.4–1.4 M). R_p vs. $[M]^2$ is linear with zero intercept (Figure 4) and, therefore, the order with respect to [M] was two. A very peculiar observation was noticed with further increase in monomer concentration. There is a regular drift in the nature of the curve at higher monomer concentrations and this was noticed in the cases of all the temperatures studied. After a particular concentration of the monomer, the slight fall in the rate is probably due to the excess monomer acting as a good solvent for the polymer. This is in line with the explanation advanced by Norrish and Smith[19] to explain the difference in kinetic behavior in good and bad solvents. According to them, a good solvent increases the mobility of the growing chain, thus increasing the probability of binary collision necessary for termination and hence the rate decreases.

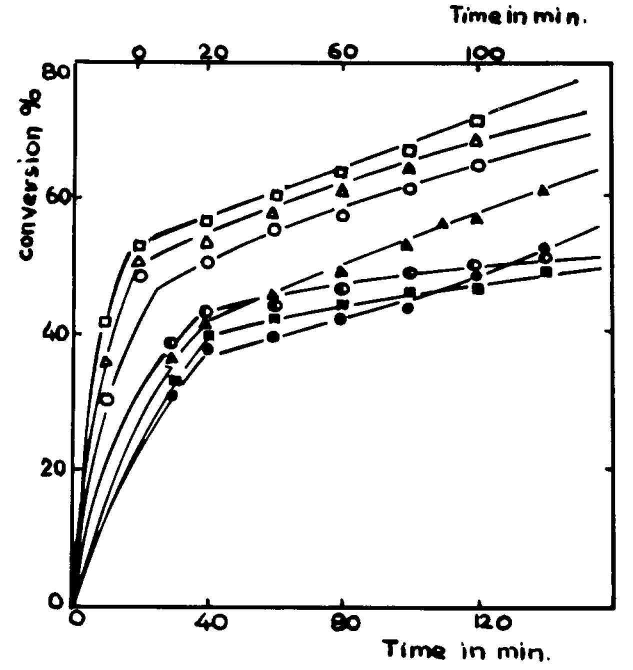

Figure 1. Polymerization of acrylamide–V(V)–cyclohexanone system. Time conversion curves at different [CH]: [V(V)] = 0.03 M, $[H^+]$ = 3.45 M, μ = 3.6 M, [AM] = 0.2 M; temperature 40 °C. (a) (○) [CH] = 0.2 M; (△) [CH] = 0.3 M; (□) [CH] = 0.4 M. (b) [CH] = 0.3 M: (◐) 5% dioxane; (●) 5% acetone; (▲) 5% acetic acid; (■) 5% dimethylformamide.

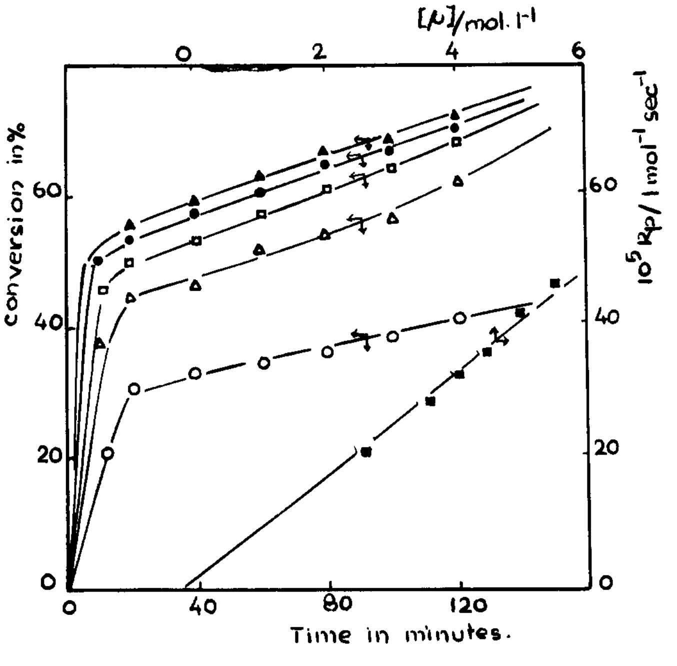

Figure 2. Polymerization of acrylamide–V(V)–cyclohexanone system. (a) Time conversion curves at different $[H_2SO_4]$ and comparison with $[HClO_4]$ and $[HNO_3]$: [V(V)] = 0.03 M; [AM] = 0.2 M; [CH] = 0.3 M; temperature 40 °C. (□) $[H_2SO_4]$ = 3.45 M; (●) $[H_2SO_4]$ = 4.35 M; (▲) $[H_2SO_4]$ = 5.25 M; (△) $[HClO_4]$ = 3.45 M; (○) $[HNO_3]$ = 3.45 M. (b) (■) Variation of rate with ionic strength: [V(V)] = 0.03 M; $[H^+]$ = 3.45 M; [CH] = 0.3 M; [AM] = 0.8 M; temperature 40 °C.

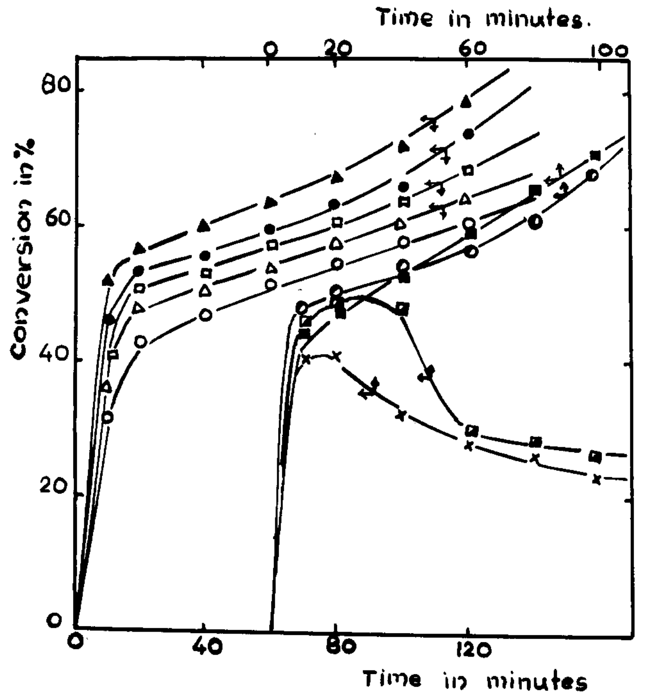

Figure 3. Polymerization of acrylamide–V(V)–cyclohexanone system. (a) Time conversion curves at different [V(V)]: $[H^+]$ = 2.95, μ = 3.0 M; [CH] = 0.3 M; [AM] = 0.2 M; temp = 40 °C. (■) [V(V)] = 0.01 M; (◑) [V(V)] = 0.03 M; (□) [V(V)] = 0.04 M; (×) [V(V)] = 0.06 M. (b) Time conversion curve at different temperatures: [V(V)] = 0.03 M, $[H^+]$ = 3.45 M; μ = 3.6 M; [CH] = 0.3 M; [AM] = 0.2 M. (○) 30 °C; (△) 35 °C; □) 40 °C; (●) 45 °C; (▲) 50 °C.

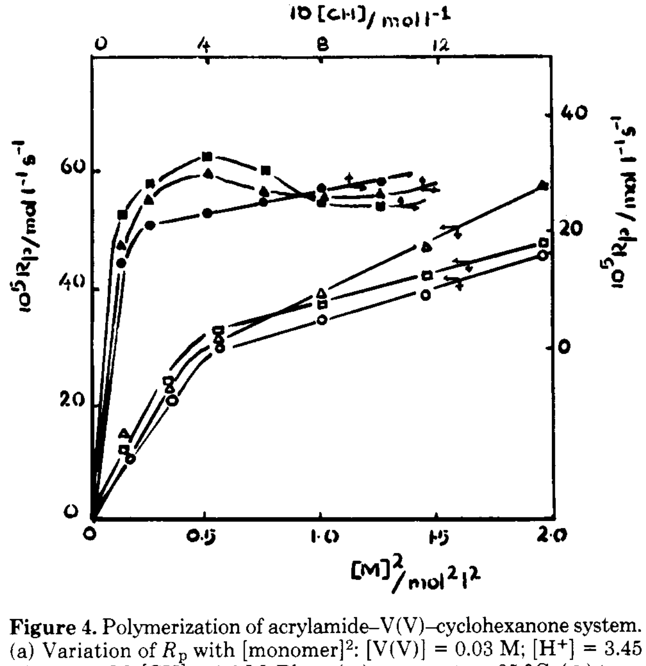

Figure 4. Polymerization of acrylamide–V(V)–cyclohexanone system. (a) Variation of R_p with $[\text{monomer}]^2$: [V(V)] = 0.03 M; $[H^+]$ = 3.45 M; μ = 3.5 M; [CH] = 0.3 M. Plots: (△) temperature 35 °C; (○) temperature 40 °C; (□) temperature 45 °C. (b) Variation of R_p with [CH]: [V(V)] = 0.03 M; $[H^+]$ = 3.45 M; μ = 3.5 M; [AM] = 0.8 M. Plots: (●) temperature 35 °C; (▲) temperature 40 °C; (■) temperature 45 °C.

The increase in monomer concentration had no effect upon the rate of disappearance of vanadium ion concentration ($-R_v$). This is contrary to the observation noted in the case of ceric ion initiated polymerization.[20-22] This also clearly indicates that quinquevalent vanadium itself cannot initiate polymerization as compared to cerium(IV) which in the absence of any reducing agents initiates polymerization. Although both V(V) and cerium(IV) are one-electron oxidants, the oxidation potential of cerium(IV) is much higher than vanadium(V),[23] for which ceric ion is capable of initiating vinyl polymerization in the absence of a reducing agent.

Rate Dependence on Acid Concentration. The effect of

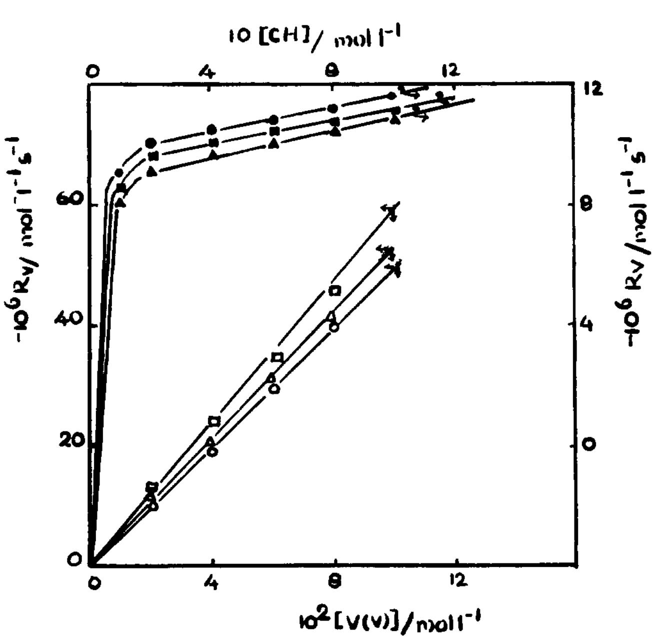

Figure 5. Polymerization of acrylamide–V(V)–cyclohexanone system. (a) Variation of $-R_v$ with [CH]: [V(V)] = 0.03 M; [H$^+$] = 3.45 M; μ = 3.5 M; [AM] = 0.8 M. Plots: (●) temperature 35 °C; (▲) temperature 40 °C; (■) temperature 45 °C. (b) Variations of $-R_v$ with [V(V)]: [H$^+$] = 3.45 M; μ = 3.5 M; [AM] = 0.8 M; [CH] = 0.3 M. Plots: (○) temperature 35 °C; (△) temperature 40 °C; (□) temperature 45 °C.

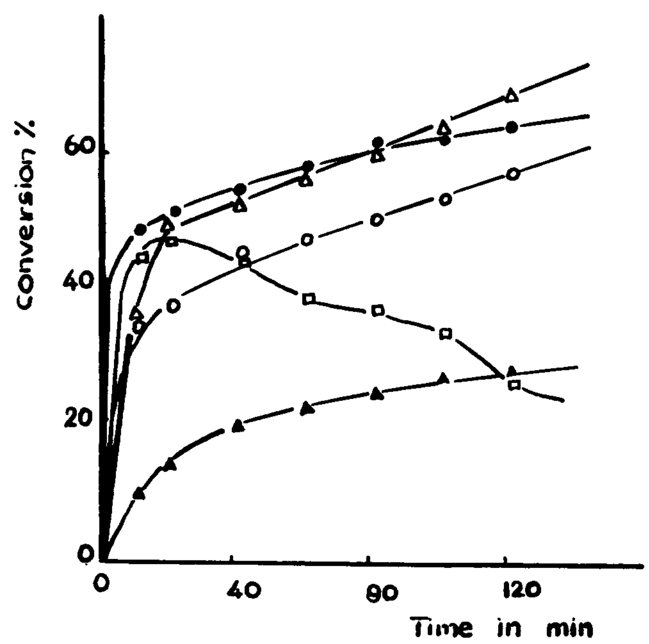

Figure 6. Polymerization of acrylamide–V(V)–cyclohexanone system. Variation of rate with time. Effect of 0.02 M neutral salts: [V(V)] = 0.03 M; [H$^+$] = 3.45 M; μ = 3.6 M; [CH] = 0.3 M; [AM] = 0.2 M; temperature 40 °C. Plots: (○) KCl; (□) Na_2SO_4; (▲) $CuSO_4$; (●) $MnSO_4$.

H_2SO_4, $HClO_4$, and HNO_3 on the percentage of conversion is shown in Figure 2. The initial rate as well as the percentage of conversion increases with increase in H_2SO_4. The order of reactivities of different acids so far as percentage of conversion is concerned is as follows:

$$H_2SO_4 > HClO_4 > HNO_3$$

which has also been observed by various workers[24-26] in the case of oxidation kinetics involving quinquevalent vanadium ion. This is because of the fact that the oxidation potential of vanadium(V) is more in H_2SO_4 and less in HNO_3.

An increase in [H_2SO_4] increased the rate, the plot of $-R_v$ vs. [H_2SO_4] being linear with intercept on the ordinate. $-R_v$ was linearly related to the Hammett acidity function, H_0.

Rate Dependence on Temperature. The percentage of conversion increases with increase of temperature. , This is similar to the observation of Whitby et al.[27] that the polymerization rate of methyl vinyl ketone in aqueous solution rises with a rise in temperature in accordance with the Arrhenius theory. On the contrary, the rate of aqueous polymerization of acrylonitrile has been shown by Thomas et al.[28] not to be very dependent on the temperature.

Effect of Organic Solvents. Water miscible organic solvents such as dioxane, acetone, acetic acid, and dimethylformamide are found to depress considerably the rate of polymerization as well as the maximum conversion (Figure 1). Most probably these solvents decrease the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical and of the growing chains; these solvents increase the regulated rate of production of primary radicals which under the existing experimental conditions renders the termination rate relatively fast as compared to the rate of growth of the polymer chains as pointed out by Kern et al.[29] Further, the inter-chain hydrogen bonding which interlocks the polyacrylamide chain is not rigid (perfect), whereby the tendency of mutual termination of the polymer chain increases. Similar observations have been noted by Mishra et al.[30] in the case of aqueous polymerization of acrylamide.

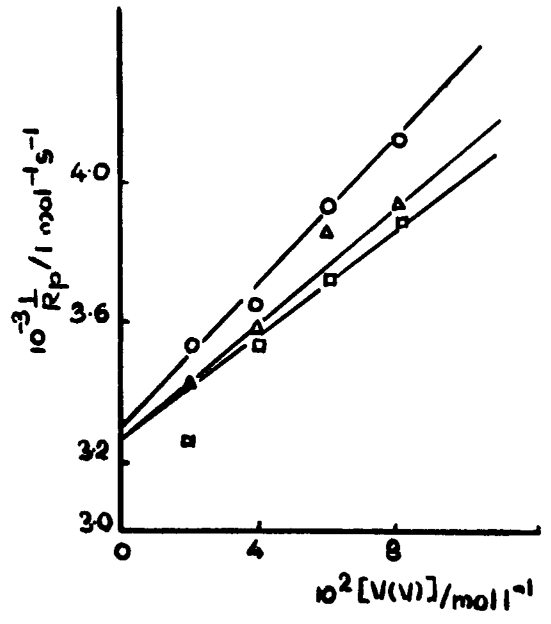

Figure 7. Polymerization of acrylamide–V(V)–cyclohexanone system: [H$^+$] = 3.45 M; μ = 3.5 M; [CH] = 0.3 M; [AM] = 0.8 M. Plots: (○) temperature 35 °C; (△) temperature 40 °C; (□) temperature 45 °C.

Effect of Inorganic Salts. The addition of neutral salts such as KCl, Na_2SO_4, and $CuSO_4$ reduces both the initial rate of polymerization and the maximum conversion to a considerable extent. This has been markedly observed in the case of Na_2SO_4. This might be due to the ionic dissociation of the added electrolyte, which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chains. On the other hand, introduction of $MnSO_4$ in small amounts into the polymerization system

Table I
Values of the Rate Parameters in the Polymerization of Acrylamide (AN) Initiated by the System Cyclohexanone/V(V)

Temp, °C	$k' \times 10^2$, l./mol s $-R_v$ vs. [V(V)]	k_p/k_t	k_0/k_i
35	2.125	0.18	33.8
40	2.55	0.16	27.7
45	3.125		25.6

brings about an increase both in the rate and the limiting conversion. This can be explained in accordance with the suggestion made by Palit et al.[18] that a disproportionation reaction occurs between V(V) and Mn(II) producing the highly reactive Mn(III) ions in the system at a rapid rate.

R_p increased with μ when $ZnSO_4$ and $NaClO_4$ were used to adjust the ionic strength and the plot of R_p vs. μ is linear (Figure 2).

Reaction Mechanism and Rate Law. The polymerization of acrylamide in aqueous media initiated by the quinquevalent vanadium ion in the presence of cyclohexanone shows characteristic features of homogeneous polymerization. In heterogeneous aqueous polymerization where the separating phase is a suspension of insoluble polymer particles and becomes thicker and thicker with the rise in catalyst concentration, the termination mechanism becomes complicated and sometimes the termination may be unimolecular or bimolecular, depending upon the concentration of the initiator.

From the proportionalities obtained between the measurable parameters and the variables, a reaction scheme has been suggested involving initiation by organic free radical produced by the interaction of V(V) with cyclohexanone and termination by V(V) ion. The termination by metal ion has been suggested in our previous communications.[10-12,31]

Taking into account the dependence of R_p on $[M]^2$ and [CH], of $1/R_p$ on [V(V)] and 1/[CH], and of $-R_v$ on [CH] and [V(V)] but not on [M], the following equations for R_p, $-R_v$, and n are suggested as has been noted by us in our previous communications.[11,12]

$$R_p = \frac{(k_p/k_t)k'[CH][M]^2}{\{[M] + (k_0/k_i)[V(V)]\}} \tag{1}$$

$$-R_v = 2k'[CH][VO_2^+] \tag{2}$$

and

$$n = (k_p/k_t)[M]/[V(V)] \tag{3}$$

The values of k_p/k_t and k_0/k_i were evaluated from eq 1 by plotting $1/R_p$ vs. [V(V)]. Taking the reciprocal of the rate expression for R_p and rearranging gives

$$1/R_p = \frac{k_t}{k_p k'[CH][M]} + \frac{k_t(k_0/k_i)[V(V)]}{k_p k'[CH][M]^2} \tag{4}$$

Plots of $1/R_p$ vs. [V(V)] according to the above equation are linear (Figure 7) and k_0/k_i values were obtained from the product (slope/intercept) × [M] and (k_p/k_t) values were obtained from the reciprocal of the product (intercept)$k' \cdot$[CH][M].

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