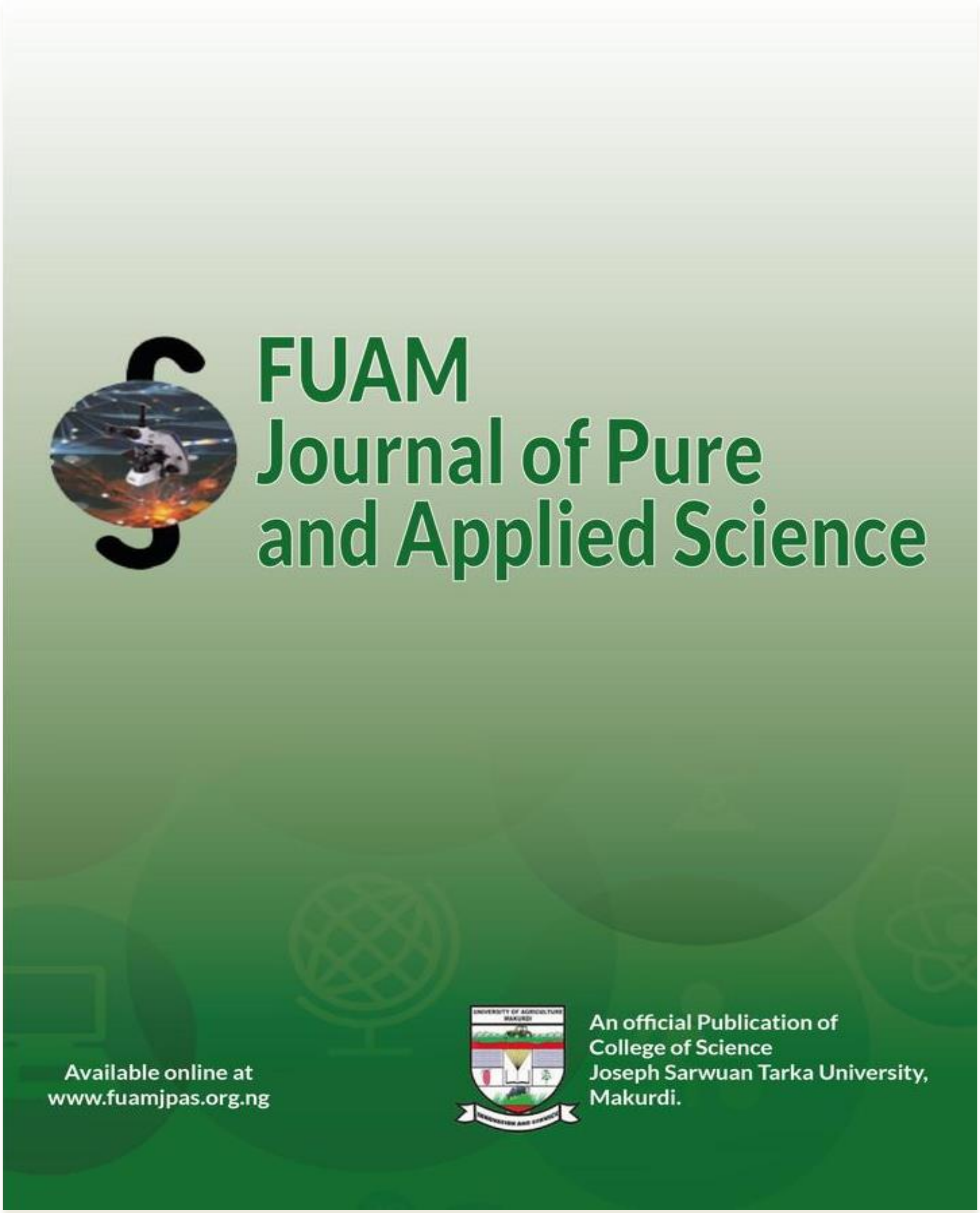
Vol. 4 No. 2, Dec. 2024



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FUAM Journal of Pure and Applied Science
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https://fuamjpas.org.ng/
Vol.4 No. 2. December, 2024

Electron Transfer Reaction between Naphthol Green B and Permanganate Ion in Aqueous Acid

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Received: 24/02/2024 **Accepted**: 27/04/2024 **Published online**: 29/04/2024

Abstract

The redox reaction between naphthol green B (NGB^{3-}) and permanganate ion has been studied in tetraoxosulphate(VI) acid medium at an ionic strength, $I = 0.50$ mol dm^{-3} (Na_2SO_4), $[H^+] = 4 \times 10^{-4}$mol dm^{-3} (H_2SO_4), T = 21 ± 1°C and $\lambda = 700$ nm. The redox reaction displayed a stoichiometry of 2:1. The reaction shows a first order dependence on [oxidant] and [reductant]. Study on the effect of ionic strength on the rate of the reaction shows that the rate of the reaction obeyed positive Bronsted - Debye salt effect; implying that the activated complex is composed of reactants of similar charges. Increased in hydrogen ion did not affect the rate of the reaction. The overall reaction conforms to the rate law: $-d[NGB^{3-}]/dt = k[NGB^{3-}][MnO_4^-]$

Addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. Added cations and anions had no effect on the rate of the reaction. Results of the Michaelis – Menten's plot gave no evidence of intermediate complex formation during the course of the reaction. Based on the results obtained, the reaction is probably proceeding through the inner-sphere mechanistic pathway.

Keywords: Intermediate; Redox; Michaelis - Menton's; Outersphere

Introduction

Electron transfer (ET) is one of the most important chemical processes in nature and it plays a central role in many biological, physical and chemical (both organic and inorganic) systems. It is a mechanistic description of a redox reaction, wherein the oxidation state of reactant and product changes. Numerous biological processes involve ET reactions. These processes include oxygen binding, photosynthesis, respiration, and detoxification. Additionally, the process of energy transfer can be formalized as a two-electron exchange (two concurrent ET events in opposite directions) in case of small distances between the transferring molecules. The reactions commonly involve transition metal complexes[1].It is well established in inorganic electron transfer reactions that electron transfer processes must be preceded by the reorganization of the solvation (also called hydration) shells surrounding reactants [2].It was Libby [3] who accounted for this phenomenon based on the Franck-Condon principle, suggesting that, before the fast electron transfer can occur, the slower nuclear rearrangements of water molecules in the hydration shells must take place, the proton being 1,836 times as massive as the electron [4]. In this study, there is need for thorough investigation of the redox reaction between naphthol green B dye with permanganate ion in aqueous acid.

Permanganate is the general name for a chemical compound containing the tetraoxomanganate(VII) ion, (MnO_4^-). Because manganese is in the +7 oxidation state, the permanganate(VII) ion is a strong oxidising agent. The ion has a tetrahedral geometry [5]. Permanganate solutions are purple in color and are stable in neutral or slightly alkaline media. The exact chemical reaction is dependent upon the organic contaminants present and the oxidant utilized. For example, trichloroethane ($C_2H_3Cl_3$) is oxidised by sodium permanganate to form carbon(IV) oxide, manganese(IV) oxide, sodium ion, hydronium ion and chloride ions.Permanganate can be produced by oxidation of manganese compounds such as manganese chloride or manganese sulphate by strong oxidising agents, for instance, sodium hypochlorite or lead dioxide [6].Despite the rich chemistry of permanganate ions, its redox reaction with NGB^{3-}has not been comprehensively documented. The aim of this work is to investigate the detail redox reaction of

$NGB^{3-}$with permanganate ion in aqueous acid and to propose its reaction mechanism.

Experimental

Materials

All chemicals and reagents used in this work were analar grade and were used without further purification. $KMnO_4$ was used as the oxidant, H_2SO_4 was used to furnish H^+ to the reaction and Na_2SO_4 was used to maintain a constant ionic strength. Acetone was used to vary the dielectric constant of the reaction medium. NGB^{3-}, the oxidant and the other reagents were prepared with distilled water. The λ_{max} (700 nm) used for this work was determined by running the spectrum of the dye solution using UV-2500PC series in the wavelength range 400 – 700 nm.

Methods

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method [7]. This was accomplished by measuring the absorbance of solutions containing varying concentrations of permanganate ion in the range $(4.0 - 8.0) \times 10^{-4}$) moldm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ moldm^{-3} and $I = 0.50$ moldm^{-3} at $\lambda = 700$ nm until a constant absorbance was obtained. A point of inflection on the curve of the absorbance versus mole ratio plot corresponds to the stoichiometry of the reaction.

The kinetic runs were performed under pseudo - first order conditions [8] with the concentration of permanganate ion at least 60-fold greater than that of the dye at T = 21 ± 1°C and ionic strength of reaction medium, $I = 0.50$ mol dm^{-3} (Na_2SO_4). The reaction was monitored spectrophotometric ally by measuring the absorbance at 700 nm using UV-Vis spectrophotometer 752. The pseudo-first order plots of log $(A_t - A_\infty)$ versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t respectively).The influence of $[H^+]$ on the rate of reaction was investigated using sulphuric acid in the range$(1.0 - 7.0) \times 10^{-4}$mol dm^{-3}, while the $[NGB^{3-}]$ and $[MnO_4^-]$ were kept constant at 21± 1°C and $I = 0.50$ mol dm^{-3} (Na_2SO_4).The effect of ionic strength of the reaction medium on the rate of the reaction was investigated in the range of 0.1 - 0.7mol dm^{-3} (Na_2SO_4) while the concentrations of other reactants were kept constant. The effect of added ions was investigated by keeping the concentration of other reactants constant while varying the ions concentrations as follows: $[X^-] = (10.0 - 80) \times 10^{-3}$mol dm^{-3}, where $X^- = (SO_4^{2-}$and $Ca^{2+})$.The inorganic product was qualitatively confirmed to be Mn^{2+} by adding 1ml of 6M HNO_3 to few drops of the solution. Sodium bismuthata was also added in a spatula and stir.

Results and Discussion

The stoichiometric study showed that two moles of the dye was consumed by one mole of the oxidant suggesting the overall equation as indicated in equation (1) below.

$$2NGB^{3-} + MnO_4^- + 3H_2O \longrightarrow 2NGB + Mn^{2+} + 5H^+ + OH + 3O_2 \quad (1)$$

Similar stoichiometry of 2:1 was reported for the redox reaction of orange II and permanganate ion in aqueous acidic medium [9]. Mn^{2+} was confirmed as the inorganic product on addition of sodium hydroxide solution. A white precipitate of manganese (II) hydroxide which was insoluble in excess sodium hydroxide solution was formed. The precipitate oxidizes on exposure to air, becoming brown as the result of formation of hydrated manganese dioxide [9].

Organic product of the reactions of NGB^{3-} with MnO_4^- gave a yellow precipitate with 2,4-dinitrophenylhydrazine, confirming the presence of carbonyl group. Ketone was further distinguished by the addition of acidified potassium dichromate, which does not change the colour of the reacting mixtures.

The constancy of k_2 values (Table 1) and Pseudo-first order plots of log (A_t-A_∞) versus time (Figure 1) were linear to more than 80% extent of the reaction, suggesting that the reaction is first order with respect to the NGB^{3-}. The order of the reaction with respect to $[MnO_4^-]$ was also determined by plotting logk_1 against log$[MnO_4^-]$ (Fig.2). Slope of one was obtained which indicate that the order of reaction with respect to $[MnO_4^-]$ is first order.

This reaction therefore conforms to the rate law:

$$-d[NGB^{3-}]/dt = k[NGB^{3-}][MnO_4^-] \quad (2)$$

Where k_2 is the second order rate constant.

Effect of changes in ionic strength of the reaction medium indicated that change in ionic strength of the reaction medium increases the rate of the reaction (Table 1). This obeyed a positive Bronsted- Debye salt effect, indicating that the activated complex is formed from reactant of similar charges.The result in Table 1 shows that increase in $[H^+]$ had no effect on the rate of chemical reaction in the range of acid investigated. The rate constants were found not to have effect on the addition of SO_4^{2-} and Ca^{2+} ions. This lack of effect by the ion suggests that the reaction might be operating through the inner – sphere pathway [10]. Addition of acrylamide to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. This shows that the participation of free radicals is unlikely. The spectrum of the reaction mixture when compared to that of the dye (NGB^{3-}) alone showed no shift in λ_{max} suggesting absence of an intermediate complex during the reaction .Plot of $1/k_1$ versus $1/ [MnO_4^{2-}]$ gave a straight line with an intercept (Figure 3). This further suggests the absence of the formation of intermediate complex thereby supporting the inner-sphere mechanism. On the basis of the above findings, the probable mechanism proposed is shown in equations 3 – 5.

Table 1: Pseudo – first order and second order rate constants for the reaction of NGB^{3-} and MnO_4^- at $[NGB^{3-}] = 5.0 \times 10^{-4}$ mol dm^{-3}, $\lambda = 700$ nm and T = 21 ± 1°C

$10^4[MnO_4^-]$, mol dm^{-3}	**$10^4[H^+]$, mol dm^{-3}**	**$10^1 I$, mol dm^{-3}**	**$10^3 k_1$, s^{-1}**	**k_2, $dm^3\ mol^{-1}\ s^{-1}$**
4.0	1.0	5.0	1.15	0.29
4.8	1.0	5.0	1.66	0.35
6.0	1.0	5.0	1.54	0.26
7.2	1.0	5.0	1.88	0.26
8.0	1.0	5.0	1.65	0.21
6.0	1.0	5.0	1.65	0.28
6.0	3.0	5.0	1.38	0.23
6.0	4.0	5.0	1.54	0.26
6.0	5.0	5.0	1.73	0.29
6.0	6.0	5.0	1.54	0.26
6.0	7.0	5.0	1.54	0.26
6.0	1.0	0.1	0.04	0.07
6.0	1.0	0.3	0.70	0.12
6.0	1.0	0.4	1.10	0.18
6.0	1.0	0.5	1.70	0.28
6.0	1.0	0.6	2.10	0.35
6.0	1.0	0.7	2.81	0.47

Table 2: Rate data for the effect of added ions (SO_4^{2-} and Ca^{2+}) on the rate of reaction of NGB^{3-} and MnO_4^- at $[NGB^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[MnO_4^-] = 6.0 \times 10^{-4}$ moldm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ moldm^{-3}, I = 0.50 moldm^{-3}, $\lambda = 700$ nm and T = 21 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	$10^3\ k_1$, s^{-1}	k_2, $dm^3\ mol^{-1}\ s^{-1}$
SO_4^{2-}	0.0	1.70	0.28
	10.0	1.38	0.23
	20.0	1.54	0.27
	40.0	1.66	0.28
	60.0	1.73	0.29
	80.0	1.44	0.24
Ca^{2+}	0.0	1.70	0.28
	10.0	1.50	0.25
	20.0	1.54	0.27
	40.0	1.66	0.28
	60.0	1.54	0.27
	80.0	1.50	0.25

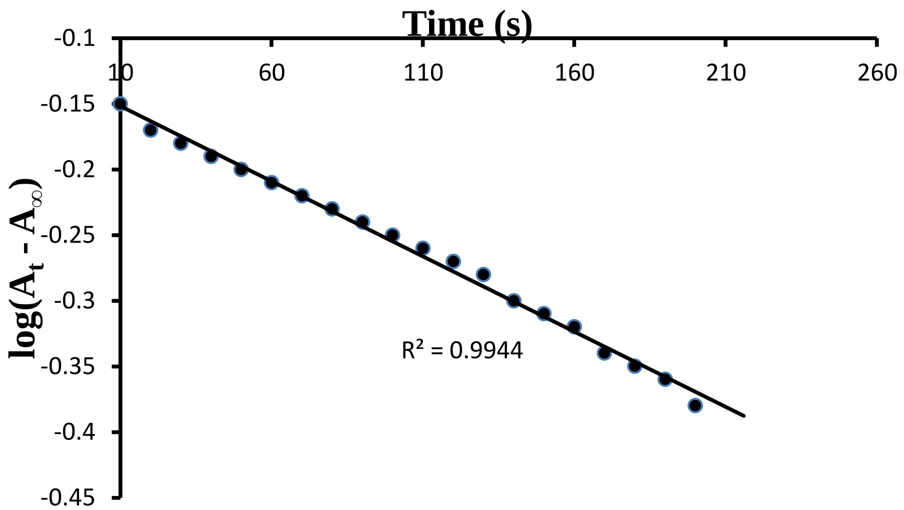

Figure 1: Pseudo-first order plot for the redox reaction of OR^- with MnO_4^- at [NGB^{3-}] = 5.0 × 10^{-5} mol dm^{-3}, [MnO_4^-] = 6.0 × 10^{-4} mol dm^{-3}, [H^+] = 1.0×10^{-4} mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 700 nm and T=21 ± 1 ^oC

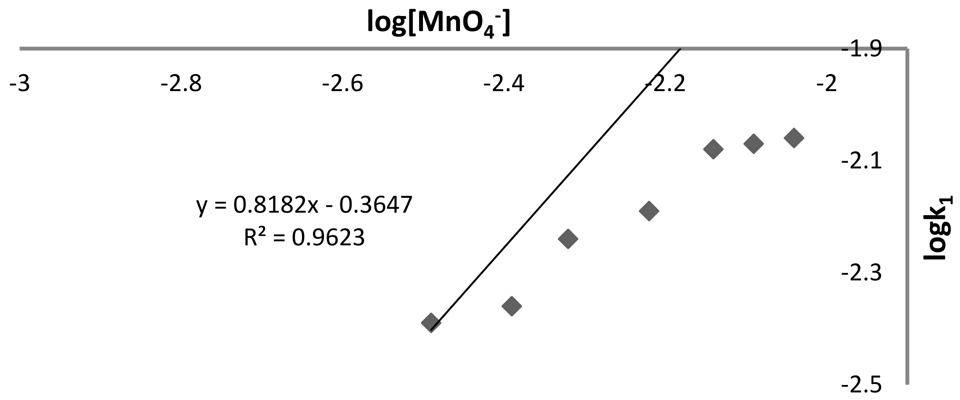

Figure 2: Plot of log k_1 versus log[MnO_4^-] for the redox reaction of NGB^{3-} with MnO_4^-at [NGB^{3-}] = 5.0 × 10^{-4}moldm^{-3}, [MnO_4^-] = (4.0 – 8.0) × 10^{-4}moldm^{-3}, [H^+] = 1.0 × 10^{-4} moldm^{-3}, I = 0.50 moldm^{-3}, λ = 700 nm and T = 21 ± 1°C

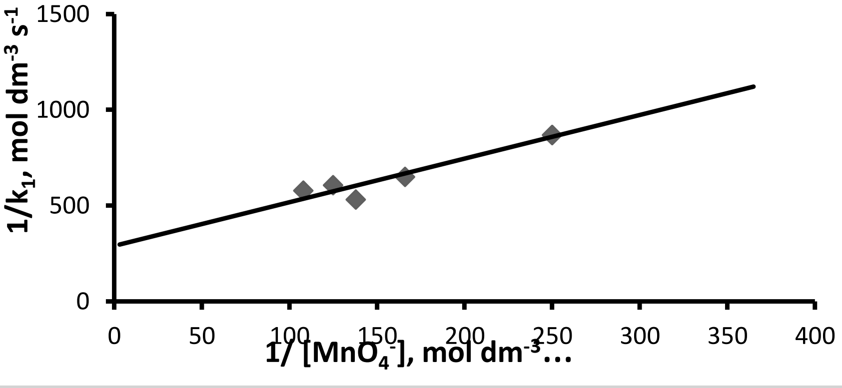

Figure 3: Michaelis - Menten plot for the redox reaction between NGB^{3-} and MnO_4^- at [NGB^{3-}] = 5.0 x 10^{-4}moldm^{-3}, [MnO_4^-] = (3.0 – 8.0) × 10^{-4}moldm^{-3}, [H^+] = 1.0 × 10^{-4}moldm^{-3}, I = 0.50 moldm^{-3}, λ = 700 nm and T= 21 ± 1°C

Reaction Mechanism

$$NGB^{3-} + MnO_4^{-} + 2H_2O \xrightarrow[\text{slow}]{k_1} NGB + MnO_2 + 4H^{+} + 2O_2 \quad (3)$$

$$NGB^{3-} + HMnO_4 \xrightarrow{k_2} Mn^{2+} + NGB + H^{+} + 2O_2 \quad (4)$$

$$\text{Rate} = k_1\{NGB^{3-}][MnO_4^{-}] \quad (5)$$

Conclusion

The redox reaction of naphthol green B with permanganate ion in aqueous acidic medium showed a stoichiometry of 2:1, a first order was observed for NGB^{3-} and MnO_4^{-} respectively. The rate of reaction showed lack of hydrogen ion dependence in acid range investigated. Added ions showed no effect on the rate of the reaction. An intermediate complex was absent during the course of the reaction, It is therefore, proposed that the reaction is operating through the inner-sphere mechanism.

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Cite this article

Myek B, Timothy P.A., Adetoro A., Anweting I.B. & Orijajogun J.O. (2024). Electron Transfer Reaction between Naphthol Green B and Permanganate Ion in Aqueous Acid. FUAM Journal of Pure and Applied Science, **4**(**2**):1-5