

Oxidation of Indole - 3 - Propionic Acid by Peroxodisulphate in T - Butanol - A Kinetic Study

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ABSTRACT

Kinetic investigation on the oxidation of Indole - 3 - Propionic acid by Peroxodisulphate in t - Butanol, have been studied in the effect of temperature, solvent, ionic strength, stoichiometry of the reaction and to the influence of radical scavengers and to find the nature of the species involved in the oxidation process. Indole and its derivatives are important class of bio - organic molecules exhibit a wide range of reactivity such as oxidation, nitration, electron transfer, substitution in many cases. It has much attention because they have antibacterial, antitumor, antifungal and anti tuberculosis properties etc., since biological oxidation form an integral component research, the present research work focus on the oxidation of certain Indole derivative by peroxodisulphate which has been proved to be a good oxidant.

Keywords : Oxidation, Kinetic Study, Indole - 3 - Propionic Acid.

I. INTRODUCTION

The kinetic study of oxidation of organic compounds is an useful and powerful method in physical organic chemistry. The study of mechanisms of oxidation reactions has been a subject of major importance to many chemists and the elucidation of reaction mechanism is undoubtedly one of the most fascinating problems in chemistry. The most important in deciding the reaction mechanism is the investigation of reaction kinetics of chemical reactions. The problems to be solved in any kinetic investigation are :to establish the relationship between the rate and various factors such as concentration of the reactants, temperature, reaction medium etc., interpretation of the empirical rate law proposed in terms of reaction mechanism, incorporating the possible intermediate and the product formed in the reaction. Viewing from the multi - faceted applications it is clear that an

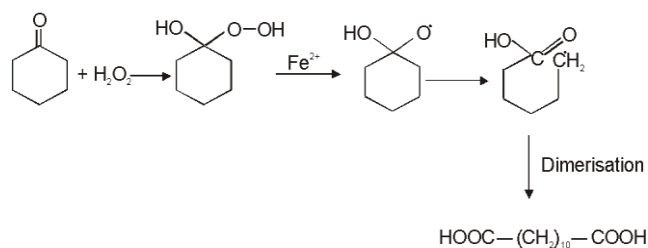
investigation of the kinetics and mechanism of redox reactions is an important one. It will not only help to enlighten the pathway of a particular reaction but also to identify newer reactions and hence the associated mechanism. In a redox reaction, the reductant may be a metal ion or metal complex in its low valence state such as Fe^{2+} , Mn^{2+} , $\text{Fe}(\text{CN})_6^{4-}$ etc., or organic compound containing oxidisable groups like aldehyde, alcohol, amine or a facile pi-system (double bond). The oxidant may be a metal ion or metal complex in its higher valence state like Ce^{4+} , Mn^{3+} , Mn^{7+} , Cr^{6+} , V^{5+} , etc., or compounds containing peroxo linkage, $-\text{O}-\text{O}-$, such H_2O_2 , HSO_5^- , $\text{S}_2\text{O}_8^{2-}$, $\text{P}_2\text{O}_8^{4-}$, $\text{C}_6\text{H}_5\text{CO}_3\text{H}$. Reaction rate is of great practical interest in both laboratory and industrial practice. No reaction that takes years to become sensibly complete is useful in making its products, but reactions that are complete in fraction of a second include hazardous explosions. It is clearly necessary to understand the factors controlling the rate atleast to some extent

before a reaction becomes useful on almost any scale.²² A study of reaction mechanism allows a more informed extension of the scope of the reaction to new but mechanistically related cases.²² One important outcome of mechanistic studies has been the chemistry of unstable intermediates of compounds that are normally not isolable. Thus, it is clear that a study of reaction mechanism of electron transfer reactions is of much significance.

PEROXIDES OF OXIDANT

Peroxides or peroxy compounds have wide applications and are used for bleaching hair and wood pulp, as rocket fuel, as oxidants in synthesis and as initiators in many polymerization reactions.²³ These are compounds having weak peroxy (-O-O-) linkage, with dissociation energy²⁴ ranging from 210 kJ mol⁻¹ for H₂O₂ to about 100 kJ mol⁻¹ for compounds barely stable at room temperature. The low bond energy is attributed to repulsion between the non-bonding electron pairs on the adjacent oxygen atoms²⁵. The peroxides are known to be good oxidants capable of accepting electrons as indicated by the high to very high oxidation potential values (E⁰), ranging from +1.19 to + 2.01 V. As a class, peroxides are characterized by the homolysis of the peroxy bond²⁶ to generate free radicals. But they also undergo -O-O- bond cleavage by polar paths, both in homogeneous²⁷ and heterogeneous phase²⁸. In the heterolytic cleavage, interestingly, the oxygen of the peroxy group usually behaves as an electrophilic and is subjected to nucleophilic displacement²⁹ on the peroxidic oxygen. Of course, reactions are known where peroxides are nucleophiles as expected of a group having lone pair of electrons. The redox reactions involving the peroxides can, therefore be classified into two types :Reactions involving homolytic cleavage of the -O-O- bond leading to the formation of free radicals as the intermediates.

Reactions following either electrophilic or nucleophilic polar path way by cleaving the peroxy bond heterolytically.



CHEMISTRY OF PEROXODISULPHATE(PDS)

Peroxy or peroxy compounds are those containing -O-O- linkage similar to that in hydrogen peroxide. There are two peroxy acids of sulphur, peroxomonosulphuric acid, H₂SO₅ (Caro's acid) and peroxodisulphuric acid, H₂S₂O₈ (Marshall's acid). Since the discovery of persulphuric acid (peroxodisulphuric acid, H₂S₂O₈) in 1878 by Berthelot,³⁰ numerous papers have appeared concerning the properties and reactions of peroxodisulphuric acid and peroxodisulphates.³¹ Peroxodisulphuric acid was synthesised by the gradual addition of calculated amount of anhydrous hydrogen peroxide to well cooled chlorosulphonic acid.³²

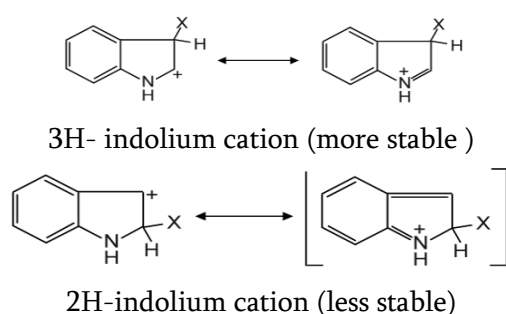


Based on the structural similarities, peroxomonosulphate, HSO₅⁻ (PMS) can be considered as a precursor of peroxodisulphate, S₂O₈²⁻, with which numerous investigations have been carried out.^{23,33-35} Both these peroxy acids can be considered as the substituted hydrogen peroxide, replacing one or both the hydrogen in hydrogen peroxide by SO₃ group. Peroxomonosulphuric acid and peroxodisulphuric acid, as well as their salts are strong oxidizing agents. They are distinguished from hydrogen peroxide by their failure to react with potassium permanganate. Iodine is liberated at once

from potassium iodide by H_2SO_5 but only slowly by $\text{H}_2\text{S}_2\text{O}_8$.

CHEMISTRY OF INDOLE

Indole was first prepared in 1866 by zinc dust distillation of oxindole. The word indole derived from the word India, a blue dye imported from India became known as indigo in the 16th century and chemical degradation of this gave rise to indoxyl, oxindole, and then to indole. Indole is a colourless crystalline solid with naphthalene like odour, a close relationship exists between the chemistry of pyrrole and of indole. Both heterocyclics are essentially non-basic, subject to easy electrophilic attack with very similar degrees of reactivity and resistant to substitution by nucleophilic reagents. The main difference is to be found in the position of greatest susceptibility to electrophilic substitution, which in pyrroles is at an α -position and in indole is at C_3 .⁸¹ It is obvious that the preferred C_3 reactivity of indoles is the direct consequence of the presence of a benzene ring. This makes 3H-indolium cations much stabler than 2H-indolium cations, for in the latter the canonical structure with the positive charge on the nitrogen is non-benzenoid.



Indole and its derivatives are important class of bio-organic molecules exhibit a wide range of reactivity such as oxidation, nitration, electron transfer, substitution in many cases. It has received much attention because they have : Antibacterial, Antiallergic, Antitumour, Psychotropic, Anti-inflammatory, Antifungal, Antitubercular

properties ,Act as human growth hormone,Many alkaloids contains indole nucleus as basic structural unit.,Have important role in the biochemical processes involved in the activity of the central nervous system. In particular indole -3- butyric acid act as phytohormone. Since biological oxidation form an integral component in research, the present work focuses on the oxidation of certain indole derivative by peroxodisulphate which has proved to be a good oxidant.

Scope of this present investigation: The objectives of this present investigation are determination of order of the reaction with respect to the reactants viz., the oxidant and substrate. Study of the effect of H^+ on the rate of reaction, effect of temperature and to understand the effect of solvent, ionic strength and stoichiometry of the reaction.

II. MATERIALS AND METHODS

CHEMICALS

Indole-3-propionic acid (Qualigens, India) of highest purity grade available was used as such without further purification. Potassium iodide, sodium thiosulphate, sulphuric acid, acrylamide, sodium bisulphate, t-butanol and starch used were all analytically pure grade samples. Acrylamide monomer was recrystallised from chloroform before use.

Potassium peroxodisulphate

The sample of potassium peroxodisulphate (SD's AR grade) was recrystallised⁸² from double distilled water and then used. The standard solutions of peroxodisulphate (oxidant) were prepared from double distilled water and it was standardised by titrating against standard sodium thiosulphate solution, iodometrically periodically.

Experimental setup

Experiments were carried out in the temperature range 25-35°C and the desired temperature were maintained by means of an electrically operated thermostat (Tohshniwal, India) with a jumo contact thermometer (Germany) working in conjunction with an electronic relay which maintain temperature accurately with an accuracy of $\pm 0.1^\circ\text{C}$. The thermostat was filled with water and it was covered with a layer of thermocole bits to minimize heat and water loss due to radiation.

The reaction vessels and standard flask were blackened from outside to avoid any photochemical reactions. The volumetric apparatus pipettes, burettes and standard flasks were standardized by usual methods⁸³

Kinetic Conditions

The Kinetic runs of the system indole-3-propionic acid was carried out in 40% aqueous t-butanol (v/v). The reactions studied were conducted under pseudo-first order conditions. The concentration of indole-3-propionic acid (substrate) was at least ten times in excess over that of the oxidant peroxodisulphate. The concentration of peroxodisulphate was varied from 1.0×10^{-3} to 3.0×10^{-3} mol dm^{-3} and that of the substrate indole-3-propionic acid was varied from 2.0×10^{-2} to 4.0×10^{-2} mol dm^{-3} and the temperature range investigated being 30-40°C. The effect of $[\text{H}^+]$ 0.40 to 0.60 mol dm^{-3} and the effect of ionic strength (μ) 1.6 to 2.2 mol dm^{-3} on rate was also investigated. The effect of dielectric constant on the reaction rate was studied by varying the percentage of t-butanol in the range 40-55% (v/v). RATE MEASUREMENT

In a typical experiment, calculated volume of NaHSO_4 (to maintain the ionic strength), H_2SO_4 , substrate, t-butanol and water were first pipetted out into the reaction vessel so that the total volume of the reaction mixture was 40 ml after the addition of peroxodisulphate. The reaction mixture was

thermostated at the desired temperature and calculated volume of peroxodisulphate from the thermostated stock solution was pipetted out into the reaction mixture. The reaction was followed by estimating the unreacted peroxodisulphate as a function of time by the modified iodometric method of Kolthoff and Carr.⁸⁴ Suitable aliquots of the reaction mixture were withdrawn at known intervals of time and transferred quantitatively into a conical flask containing approximately 10% potassium iodide solution 10 ml, 10% potassium nitrate solution 5 ml and allowed to stand for 30 minutes in dark. The liberated iodine was titrated against standardised sodium thiosulphate solution using starch as an indicator. The amount of the peroxodisulphate unreacted, $[\text{peroxodisulphate}]_t$ was thus determined from the kinetic runs. The pseudo-first order rate constant, $k'(s^{-1})$ was evaluated from the slopes of the plots of $\log [\text{peroxodisulphate}]_t$ vs time (min) by the method of least-squares, $k'(s^{-1}) = \text{slope} \times 2.303 / 60$. All the pseudo-first order plots were linear with a correlation coefficient of 0.996 - 0.999. It was checked that the results were reproducible within an accuracy of $\pm 5\%$. The second order rate constants, k_2 mol⁻¹ dm³ s⁻¹ were evaluated from the relation $k_2 = k' / [\text{indole-3-propionic acid}]$.

III. RESULTS AND DISCUSSION

Factors influencing the rate of oxidation of indole-3-propionic acid by peroxodisulphate such as effects of $[\text{peroxodisulphate}]$, $[\text{Indole-3-propionic acid}]$, $[\text{H}^+]$ ionic strength (μ), dielectric constant and temperature have been studied. Rate and activation parameters were evaluated.

Effect of $[\text{peroxodisulphate}]$

To establish the dependence of rate on $[\text{peroxodisulphate}]$, the oxidant used in this work was performed by varying the concentration of $[\text{peroxodisulphate}]$ over the range 1.0×10^{-3} mol dm^{-3} to 3.0×10^{-3} mol dm^{-3} Table 1, Figure 1. While

varying [peroxodisulphate] the other parameters like [indole-3-propionic acid], $[H^+]$, percentage of aqueous t-butanol (solvent) and ionic strength (μ) were all kept constant. The values of pseudo-first order rate constant k' (s^{-1}) obtained were shown in the Table 1. From this table, it may be inferred that the values of k' (s^{-1}) remain constant for different [peroxodisulphate]. This observation indicates the first order dependence of reaction rate on [peroxodisulphate]. Further, first order with respect to [peroxodisulphate] was confirmed from the linear plots of log rate vs log [peroxodisulphate] Figure 2 with slope almost very close to Unity. Such a first order dependence of rate on [peroxodisulphate] in many studies have been reported.⁴⁹⁻⁵³

Effect of [indole-3-propionic acid]

The dependence of reaction rate on [indole-3-propionic acid] was studied with fixed [peroxodisulphate], $[H^+]$, ionic strength (μ) and solvent composition (aqueous t-butanol) but varying the initial concentration of indole-3-propionic acid over the range 2.0×10^{-2} mol dm^{-3} to 4.0×10^{-2} mol dm^{-3} . It was found that the rate increases with increase in [indole-3-propionic acid], tables 2,3 and 4, Figure 3. This indicates that the reaction obeys first order with respect to [indole-3-propionic acid]. First order dependence of rate on [indole-3-propionic acid] was confirmed by the linear plot of log rate vs log [indole-3-propionic acid] with slope almost very close to unity, Figure 4. The values of k' (s^{-1}) when plotted against [indole-3-propionic acid] yielded a straight line passing through origin, Table 5, Figure 5 also confirms the first order dependence of rate on [indole-3-propionic acid] and also the absence of any self decomposition of the oxidant, peroxodisulphate as was already observed in earlier works^{43,49-53,55}. The observation of total second order kinetics that is first order each with respect to [peroxodisulphate] and [indole-3-propionic acid] proves that the mechanism involves an ionic route as already established in peroxodisulphate oxidations^{43,49-53,55}

Effect of $[H^+]$

There action rates measured at fixed [peroxodisulphate], [indole-3-propionic acid], ionic strength (μ) and percentage of aqueous t-butanol but with different initial concentrations of $[H^+]$ (0.40 to 0.60 mol dm^{-3}) was found to be the same, Table 6, Figure 6. This observation indicates a zero order dependence of rate on $[H^+]$. This kinetic behavior indicates the non existence of any protonation equilibrium with respect to both peroxodisulphate and indole-3-propionic acid under the present experimental conditions employed. Such a similar observation was noticed in the oxidation reaction of certain alkyl indoles by peroxo oxidants⁵¹.

Effect of ionic strength (μ)

There action rates measured at fixed [peroxodisulphate], [indole-3-propionic acid], $[H^+]$ and percentage of aqueous t-butanol but with different ionic strength (μ) values by the addition of sodium bisulphate, it was noticed that increases of μ did not alter the reaction rate significantly, Table 7. Figure 7 This observation show that either both or atleast one of the reactants should be neutral in accordance with Bronsted-Bjerrum equation.

$$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu}$$

Where,

k_0 = rate constant in absence of any added salt ie $\mu = 0$.

k = rate constant in presence of any added salt, i.e $\mu \neq 0$

Z_A & Z_B = Charge of the reactants

μ = ionic strength

Since peroxodisulphate is known to exist as $S_2O_8^{2-}$ ion, the active species of the oxidant. From this it is clear that the reductant namely the indole-3-propionic acid should be neutral. This show that the reaction occurs between a neutral species namely indole-3-propionic acid molecule and a negative ion $S_2O_8^{2-}$ the active species of the oxidant^{51,52,54}. and it is a

characteristic proof of the absence of free radical involvement.

Effect of dielectric constant

In order to determine the effect of dielectric constant (polarity) of the medium on rate, by varying the percentage of t-butanol in the reaction mixture from 40-55% (V/V) and all other parameters were kept constant. The data clearly reveals that the reaction rate was found to increase with decrease in the percentage of solvent i.e., with, increasing dielectric constant or polarity of the medium and lead to the inference that there is a charge development in the transition state involving a more polar activated complex than the reactants⁸⁵, a neutral molecule indole-3-propionic acid and a mononegative ion ($S_2O_8^{2-}$) suggesting a polar (ionic) mechanism Table 8, Figure 8.

Rate and activation parameters

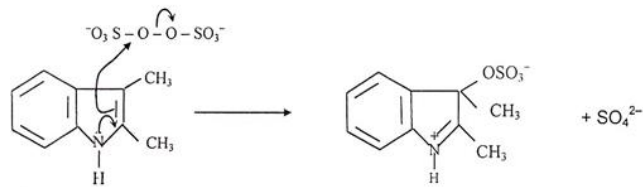
The effect of temperature on rate was studied in the range 303-313 K and the results are shown in the table 9. The Arrhenius plot of $\log k_2$ vs $1/T$ was linear, Figure 9. From the slope of the above plot, the activation energy (E_a) was calculated. Then the values of other activation parameters ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were computed from Eyring equation, Table 10.

$$k = (k_B T/h) e^{-\Delta G^\ddagger / RT}$$

where,

k	=	rate constant
k_B	=	Boltzmann constant ($1.38066 \times 10^{-23} \text{ JK}^{-1}$)
h	=	Planck constant ($6.6262 \times 10^{-34} \text{ Js}$)
ΔG^\ddagger	=	Free energy of activation
R	=	Gas constant ($8.31441 \text{ JK}^{-1} \text{ mol}^{-1}$)
T	=	Temperature (K)

The observed second order rate law and the magnitude of the activation parameters, particularly the high negative ΔS^\ddagger value are as expected according to Edwards^{86,87} for a nucleophilic displacement on the peroxide linkage as given below.



Test for free radicals

The observed total second order dependence of rate, first order each on [peroxodisulphate] and [indole-3-propionic acid] shows that the reaction involves a non-radical pathway. The peroxyanion oxidants peroxodisulphate, peroxomonosulphate etc are able to undergo free radical reaction involving the $SO_4^{\bullet-}$ as intermediate⁸⁸. It was observed that no polymer was formed when a freshly distilled acrylamide monomer was added to the deaerated reaction mixture indicating the absence of free radical intermediates.

Stoichiometry

The Stoichiometry of the reaction [indole-3-propionic acid] : [peroxodisulphate] was determined by taking an excess of peroxodisulphate over indole-3-propionic acid and allowing the reaction for completion. Since the concentration of indole-3-propionic acid taken is less compared to that of peroxodisulphate, all the substrate taken would have completely reacted leaving behind the unreacted peroxodisulphate. Based on the iodometric estimation, the amount of substrates indole-3-propionic acid and peroxodisulphate consumed, the stoichiometry of [indole-3-propionic acid] : [peroxodisulphate] was found to be 1: 2

Rate law

In accordance with the above observations, the rate equation for the disappearance of peroxydisulphate is given as

$$\text{rate} = -d[\text{PDS}] / dt = k_2 [\text{PDS}] [\text{indole-3-propionic acid}]$$

$$\text{rate} / [\text{PDS}] = k_2 [\text{indole-3-propionic acid}] = k'$$

Where,

k' = pseudo-first order rate constant

k_2 = second order rate constant

The above rate equation obey overall second order Kinetics, first order each with respect to [peroxydisulphate] and [indole-3-propionic acid] and zero order with respect to $[\text{H}^+]$.

Comparison with peroxymonosulphate

The result of this work when compared with that of peroxymonosulphate revealed certain features such as: The reaction of peroxydisulphate with indole-3-propionic acid studied proceed through ionic (polar) mechanism as in peroxymonosulphate oxidation of

indole-3-propionic acid. Further the reaction of peroxymonosulphate is faster than that of peroxydisulphate⁸⁸ with indole-3-propionic acid. The lower reactivity of peroxydisulphate was attributed due to steric hindrance caused by the presence of two SO_3 groups on both sides of the $-\text{O}-\text{O}-$ linkage⁸⁹ in peroxydisulphate ion ($\text{S}_2\text{O}_8^{2-}$), even though the redox potential of peroxydisulphate ($E^\circ = 2.01\text{V}$)⁹⁰ is higher than that of peroxymonosulphate ($E^\circ = 1.82\text{V}$)⁹¹. A similar trend was observed in the oxidation of a number of other substrates like halide ions⁹², acetophenone semicarbazone⁵⁰, aliphatic aldehydes⁹³ and aromatic aldehydes⁹⁴ by peroxymonosulphate

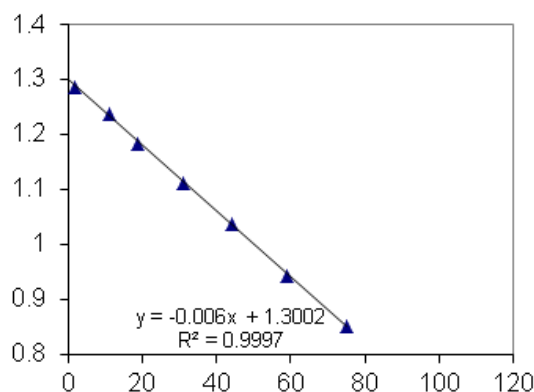


Figure 1

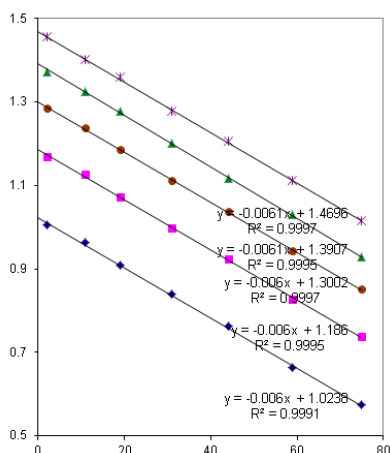


Figure 2

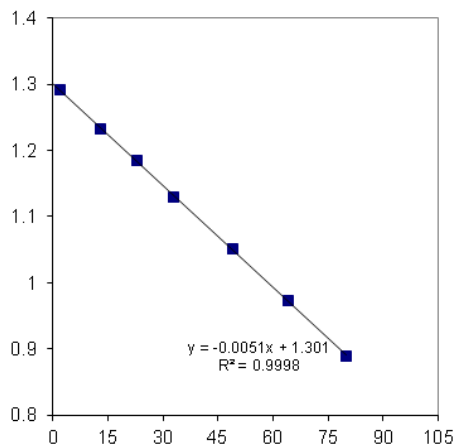


Figure 3

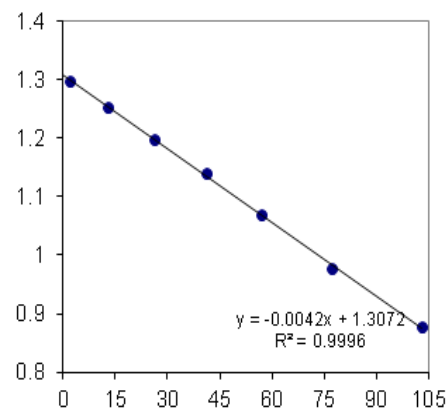


Figure 4

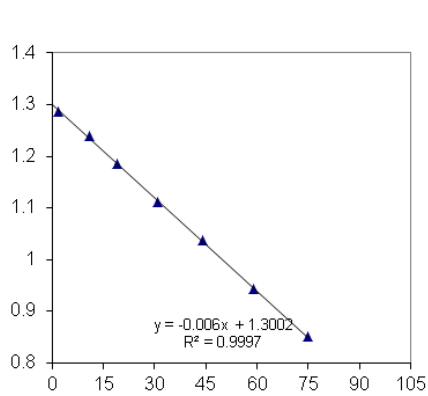


Figure 5

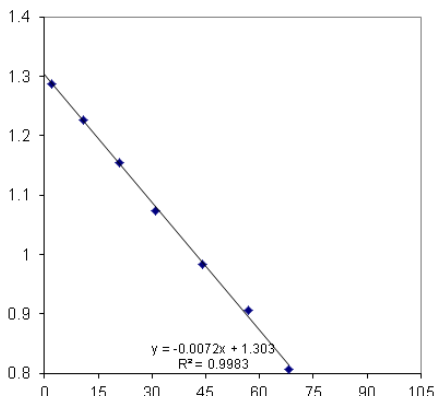


Figure 6

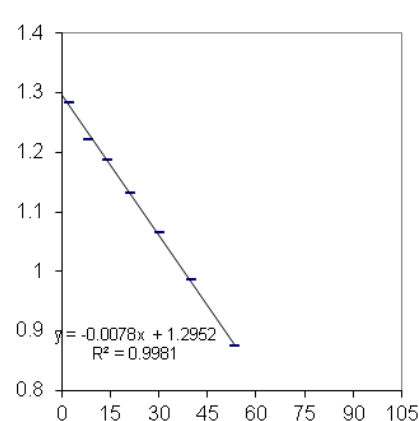


Figure 7

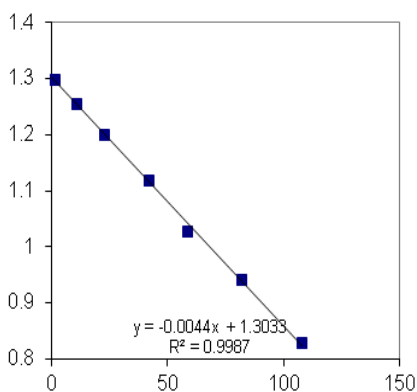


Figure 8

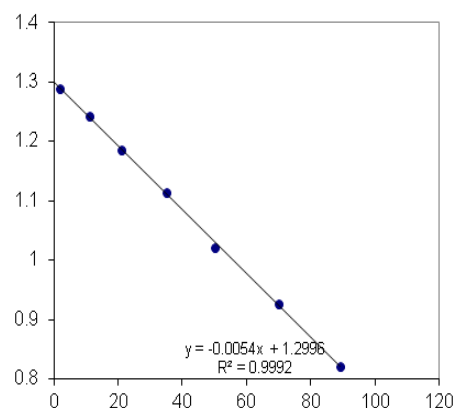


Figure 9

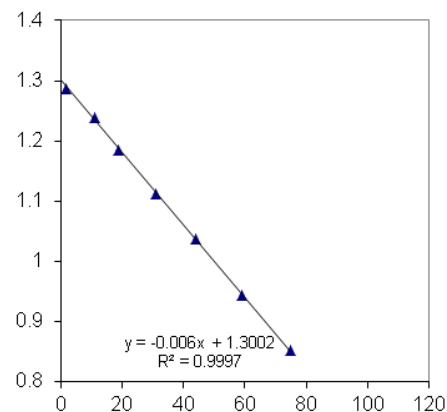


Figure 10

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