

KINETICS AND MECHANISM OF OXIDATION OF 2-PENTANONE BY NICOTINIUM DICHROMATE

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ABSTRACT: - The oxidation of 2-Pentanone by Nicotinium Dichromate has been studied by spectrophotometrically in binary solvent mixture of aqueous acetic acid with NDC medium. Kinetic studies employing NDC as an oxidant and allied aspects of its reactions lead us to conclude that the activity of NDC is much limited and needs to be explored in a broad way. It possesses vital potentiality and displays interesting behaviours at moderate condition of temperature. It use can be extended in analytical, applied chemistry and in separation/ identification of organic compound. Fruitful outcome of the kinetic studies can suitably be applied in the field of pharmacology, Hi-tech, bio-chemistry, in finding the rate of growth¹⁹²⁻¹⁹⁷ of tissues and malignancy. The study will certainly enlighten the future workers in carrying out researches of great value contribution and information's through kinetic study will enrich chemical literature to a great extents.

KEYWORDS: Kinetics of Oxidation, 2-PENTANONE and Nicotinium dichromate (NDC).

INTRODUCTION

The birth of kinetics often is taken to have occurred in 1850, when the German chemist Ludwig Ferdinand Wilhelmy (1812-1864) studied the rate of inversion of sucrose¹. This pioneering work is of special significance as being the first in which a quantitative approach was made to reaction rates. Wilhelmy interpreted the course of the reaction by the use of a differential equation and also proposed an empirical equation to express the temperature dependence of the rate. Wilhelmy's work remained almost unnoticed for over 30 years, after which Friedrich Wilhelm Ostwald² ((1853-1932) called attention to it.

Long before Wilhelmy carried out his work, even as early as the 18th century, some measurements had been made of rates of chemical reactions. For example, in 1777 C.F. Wenzel³ described some measurements of the rate of solution of metals in acids but gave no details, merely saying that the rate increased with increasing concentration of acid. In 1818 the French chemist Louis Jacques Thenard⁴ (1777-1857) studied the rate of decomposition of hydrogen peroxide, a substance he had

discovered. However, none of these early studies made much of a quantitative attack on the problem of reaction rates. The early chemists were largely concerned with discovering new substances and not so much with interpreting chemical behavior. It was only in the second half of the 19th century that physical methods began to be applied to chemical problems and that investigations were carried out in the branch of science now known as physical chemistry.

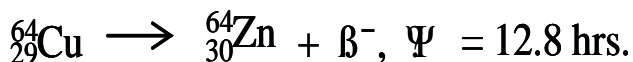
Since then the significance of chemical kinetics came in existence. Chemical kinetics is a branch of chemistry, which deals with the measurement of the rate of chemical reactions. An ideal theory of chemical kinetics would start with the time dependent equation, which could be solved to predict the rates of such simple physical and chemical processes as change in the energy state of a molecule and energy transfer reactions in which no net chemical changes occurs but energy is transferred between molecules. Livingston¹⁵ called the special attention to signifying in field of reaction mechanism as "No reaction mechanism can be considered to me more than a temporary working hypothesis until it is supported by kinetic data."

The kinetics remains one of the most important tool even this day in finding out the underline mechanism of the reaction. Thus due to developments of modern physical techniques viz. n.m.r., i.r., u.v., visible, absorption spectroscopy, mass spectra, epr. thermogravimetry, colourometry, polarography, chromatography etc. and wide and vast applicability of hi-tech, super-tech, has shed a new light and horizons on reaction mechanism and provide the complete picture of the reactions.

Modern trends of kinetics

Franclin¹⁷ introduced the electron transfer which has created a new era in the field of chemical kinetics. The oxidants based on redox reactions are of considerably academic interest and of technological importance. In 1969 A. Broido developed T.G. techniques and employed to study the kinetics of chemical reaction based on the Arrhenius equation. Recently this valuable phenomenon of kinetics is fully utilized to carry out the reaction exhibiting radioactivity¹⁸ with half-lives less than a second. The radioactive decay of ⁶⁴Cu₂₉ an

unstable nucleus is an important example of a process that follow a first-order rate law :



The laser technology, flash photolysis, rate of growth of malignancy in cancer, rate of blood circulation in body, and rate of tissues movement in bio-plants etc. applied to kinetic measurements within the range of picosecond. Yalman¹⁹ applied electronegativity and well defined oxidation state to kinetics. In 1970, Goldstein²⁰ (U.S.A.) has utilized molecular orbital theory to provide a strong evidence of changes in order of electronegativities based on redox reactions.

During the recent era it has become interesting to investigate the mechanistic path-way of redox reactions. Originally this field was little probed as the mechanism often varied greatly with the oxidizing and reducing agents employed. Oxidation of organic compounds may be represented as electron transfer, hydride transfer, H atom transfer, addition-elimination mechanism and displacement mechanism.

In the literature of organic chemistry a number of oxidizing agents have been added. Some of them are selenium dioxide, chromic acid, potassium permanganate, hydrogen peroxide, periodic acid, potassium bromate, chloramine-T, bromamine-T, potassium ferricyanide, osmium tetroxide, leadtetraacetate, bromine, thallium(III), vanadium(V), cerium(IV), NCSA, NBSA, SeO₂ etc. used in the kinetic study of organic compounds based on redox reactions.

Dichromate have been used as mild and selective oxidizing reagent in synthetic organic chemistry.¹ A variety of compounds containing Chromium (VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional group. The kinetics and mechanism involving Cr (VI) has been recently well study.

A number of new chromium containing compounds like pyridinium dichromate², chlorochromate,³ 2,2-bipyridinium chlorochromate⁴, pyridinium fluoro-chromate⁵, nicotinium fluoro-chromate⁶, nicotinium dichromate bromochromate⁷, nicotinium dichromate⁸, pyridinium fluoro-chromate⁹, imadazolium fluoro-chromate¹⁰ have been used to study the kinetics and mechanism of oxidation of various organic compounds. However, most of the reagents developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, hydroscopicity, low selectivity, long reaction time and need for large excess of reagent.

NICOTINIUM DICHROMATE AS AN OXIDANT

Several oxidizing agents, specific and selective to varying degree, have been added to the literature of oxidation of organic and inorganic compounds.

In addition to metal cation oxidants, the other group that has received much attention, now-a-days is Nicotinium dichromate have been used as mild eco-friendly and selective oxidizing reagent in synthetic organic chemistry. Selective oxidation of alcohols to their corresponding aldehydes and ketones²¹ is an important transformation in organic chemistry which has received the most attention over years, especially in the search of versatile and selective reagent for this purpose. Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry. A variety of compounds containing chromium(VI) have proved to be versatile reagents capable of oxidizing almost every oxidizing functional groups. The kinetics and mechanism of oxidation of Cr(VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates. The development of newer chromium(VI) reagents for the oxidation of organic substrates continues to be of interest.

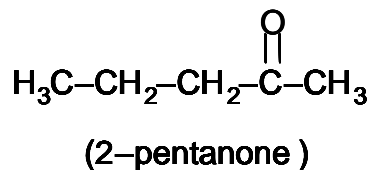
SCOPE AND IMPORTANCE OF THE PRESENT WORK

Now-a-days Nicotinium dichromate (NDC) an eco-friendly oxidant has been synthesised and employed in the oxidation of substituted.

In proposed study, 2-pentanone are actually ketones containing keto functional group at 2-carbon as, exhibited variety of chemical reaction with different oxidants viz. selenium dioxide¹¹, bromamine-T¹², NBSA¹³, Acid-bromate¹⁴, hexacyanoferrate(III)¹⁵, chromic acid¹⁶ and NCSA.¹⁷

The study of such reaction is of great significance and of interest because of its vast implication in understanding the nature of chemical processes involved.

In the present investigation, NDC has been employed as an oxidant. Thus in view of exploring the kinetics of 2-pentanone with this particular oxidant and also in order to throw light insight the reaction path, and its vital activity the 2-pentanone has been selected for oxidation study :



METHODS AND MATERIALS

All the materials used in the kinetic investigation of 2-pentanone with NDC were of analytical grade. The following procedure have been employed for the preparation of various standard solutions related to kinetic study.

Preparation of NDC solution

Nicotinium dichromate was prepared by chromium trioxide (10 g, 0.1 mol) was dissolved in distilled water (15 ml) and cooled to 0 °C. To this solution was added hydrobromic acid (17 ml, 48%) slowly with vigorous stirring, then nicotinium dichromate (13 ml, 0.1 mol) was added dropwise for 10 minutes. The reaction mixture was cooled for 2-3 h and filtered. The resulting yellow orange needles were dried and recrystallised.

Preparation of substrates solution

2-pentanone were distilled under reduced¹⁸, pressure using a trace at zinc dust during distillation. Doubly distilled water was used throughout the course of investigation. Glacial acetic acid was used as the solvent. The reactions were carried out in 10% acetic acid water (v/v) in case of each 2-pentanone. Stock solution of (H₂SO₄) sulphuric acid (B.D.H.) was prepared by diluting its appropriate volume with distilled water. The concentration of the acid was determined by titrating it against standardised sodium hydroxide solution.

Preparation of indicator solution

Starch was used as an indicator for iodometric estimation. It's solution was prepared according to method given in vogels book.

Preparation of Potassium dichromate and sodium thio- sulphate solution

The standard solution of potassium dichromate (B.D.H.) was prepared by dissolving the weighed amount of B.D.H. sample in doubly distilled water. However it was essential to prepare fresh solution as it is reported that the spectra of this solution do not alter appreciably for over a period of days or weeks even in diffused day light.¹⁹

The solution of sodium thiosulphate (B.D.H.) was prepared by taking a grade sample in distilled water and was standardised against standard CuSO₄ solution iodometrically.

The solutions of other chemicals were prepared either by direct weighing or standardising them by established methods.

Preparation of other solutions

(a)The solution of reagents of analytical grade were prepared in triply distilled water. They were used through the investigation with NDC.

(b)Binary solvent mixtures of acetic acid and water were prepared by mixing known volume of these solvents.

(c)The solution of sodium chloride, KCl (Analar and B.D.H.) potassium chloride (B.D.H.) CuSO₄ 5H₂O (B.D.H.) MnSO₄ 5H₂O (B.D.H.) and oxalic acid

(G.R.S.M.) were prepared by dissolving its calculated amount in appropriate volume of distilled water.

(d) The solution of acrylonitrile was prepared by standard method for the identification of free radicals if formed during the course of oxidation.

Experimental study

Preliminary experiments for the oxidation of 2-pentanone with NDC were conducted to choose the appropriate conditions of concentration of the reactants and temperature under which these oxidation proceeds with measurable rate.

In each set of reaction, concentration of substrate was taken in large excess over the concentration of oxidant.

Procedure

The known volume of oxidant, NDC acetic acid and other reagents were taken in a glass stoppered reaction flask and substrate solution in another vessel, made of pyrex glass which were placed in a thermostat maintained at a desired temperature with an accuracy of $\pm 0.1^{\circ}$ C. When the equilibrium of temperature is reached, the solutions were mixed and aliquot was withdrawn immediately and was quenched with ice-cold water. The amount of unreacted NDC was estimated iodometrically¹⁹⁻²² with the standard solution of sodium thiosulphate using starch as an indicator. The titre value of zero time was taken as "a". The aliquots were withdrawn at regular intervals of time and estimated for unconsumed NDC. These reading were the values of (a-x) at time "t".

The experimental data were fed into the integrated form of equation for pseudo first-order reaction.

The first-order rate constant calculated from the equation The values of rate constant obtained were found fairly constant within the experimental error ($\pm 3\%$) suggesting that each reaction follows first-order kinetics.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

RESULT AND DISCUSSION

Kinetics of oxidation of 2-pentanone have been studied in binary solvent mixture of aqueous acetic acid with NDC. The following results were obtained :

- The kinetics data have been collected for five-fold concentration of oxidant (NDC) at fixed concentration of other reactants and temperature. The linear plots of $\log (a-x)$ vs. time, suggested that the first-order rate was observed with respect to oxidant.
- The reactions follow first-order kinetics at lower concentration of substrate which tends toward zero-order at higher concentration, showing limiting value of rate constant. The substrate

understudy, obey first-order kinetics and the value of pseudo first-order constant is nearly constant. The plots of $\log(a-x)$ vs. time is linear with nearly constant slope (Fig. 1) It is therefore, concluded that the order is one with respect to oxidant.

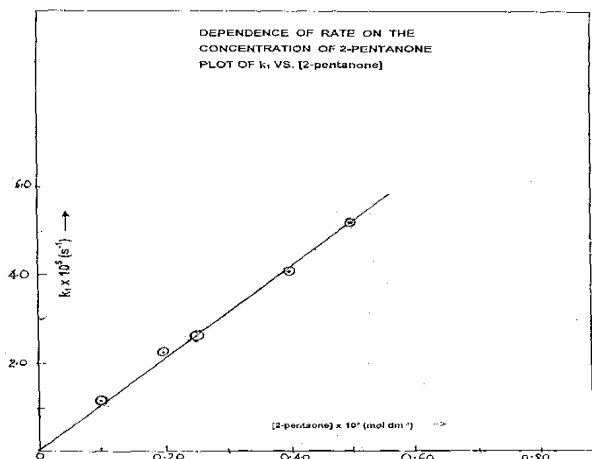


Fig. 1 [NDC] = 2.50×10^{-3} (mol dm⁻³); [H⁺] = 1.0×10^{-1} (mol dm⁻³);
 HOAc-H₂O = 50% (v/v);
 TEMP. = 303 K

Table : 1. Dependence of rate on the variation of the concentration of 2-pentanone

[NDC] = 2.50×10^{-3} (mol dm⁻³);
 [H⁺] = 1.0×10^{-3} (mol dm⁻³);
 HOAc-H₂O = 50% (v/v);
 Temp. = 303° K

Sr. No.	[2-pentanone] × 10 ³ (mol dm ⁻³)	10 ⁴ k ₁ (s ⁻¹)
1.	1.00	1.26
2.	2.00	2.35
3.	2.50	2.65
4.	4.00	4.16
5.	5.00	5.20

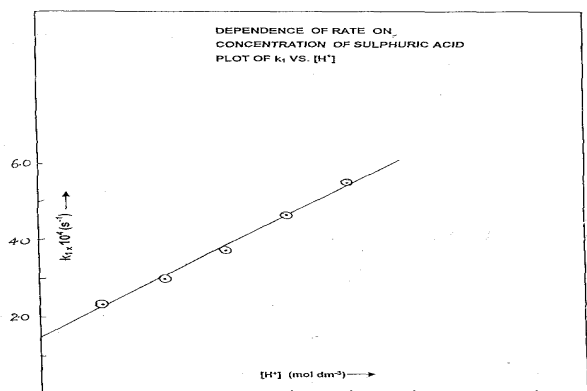


Fig. 2 [2-pentanone] = 2.00×10^{-2} (mol dm⁻³); [NDC] = 2.50×10^{-3} (mol dm⁻³);
 HOAc-H₂O = 50% (v/v);
 TEMP. = 303 K

(c) The reactions are fully acid catalyzed. The plot of k_1 vs. substrate are obtained linear with unit slope (Fig. 2) confirming that the order with respect to substrate is one

Table : 2
 Summary Dependence of rate on the concentration of Sulphuric acid

[2-pentanone] = 2.00×10^{-2} (mol dm⁻³);
 [NDC] = 2.50×10^{-2} (mol dm⁻³);
 HOAc-H₂O = 50% (v/v)
 Temp. = 303° K

Sr. No.	[H ⁺] × 10 ³ (mol dm ⁻³)	2-pentanone 10 ⁴ k ₁ (s ⁻¹)
6.	0.10	2.35
7.	0.20	3.02
8.	0.30	3.73
9.	0.40	4.71
10.	0.50	5.55

(d) The first-order rate constant increases with increasing composition of acetic acid i.e. rate slightly accelerated with decrease in dielectric constant of the medium. The plot of $\log k_1$ vs. $10^3/D$ were obtained linear with positive slope in each substrate (Fig. 3).

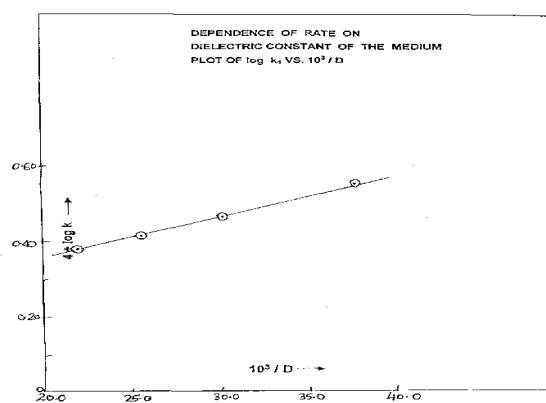


Fig. 3 [NDC] = 2.50×10^{-3} (mol dm⁻³); [2-pentanone] = 2.00×10^{-2} (mol dm⁻³);
 [H⁺] = 0.10 (mol dm⁻³);
 TEMP. = 303 K

Table: 3 Dependence of rate on dielectric constant of the medium

[2-pentanone] = 2.00×10^{-2} (mol dm⁻³);
 [NDC] = 2.50×10^{-3} (mol dm⁻³);
 [H⁺] = 0.10×10^{-1} (mol dm⁻³);

Temp. = 303° K

Sr. No.	[HOAc-H ₂ O] % (v/v)	$\frac{10^3}{D^*}$	2-pentanone $10^4 k_1$ (s ⁻¹)
1.	40	21.98	2.26
2.	50	25.64	2.35
3.	60	30.36	2.79
4.	70	38.04	3.23

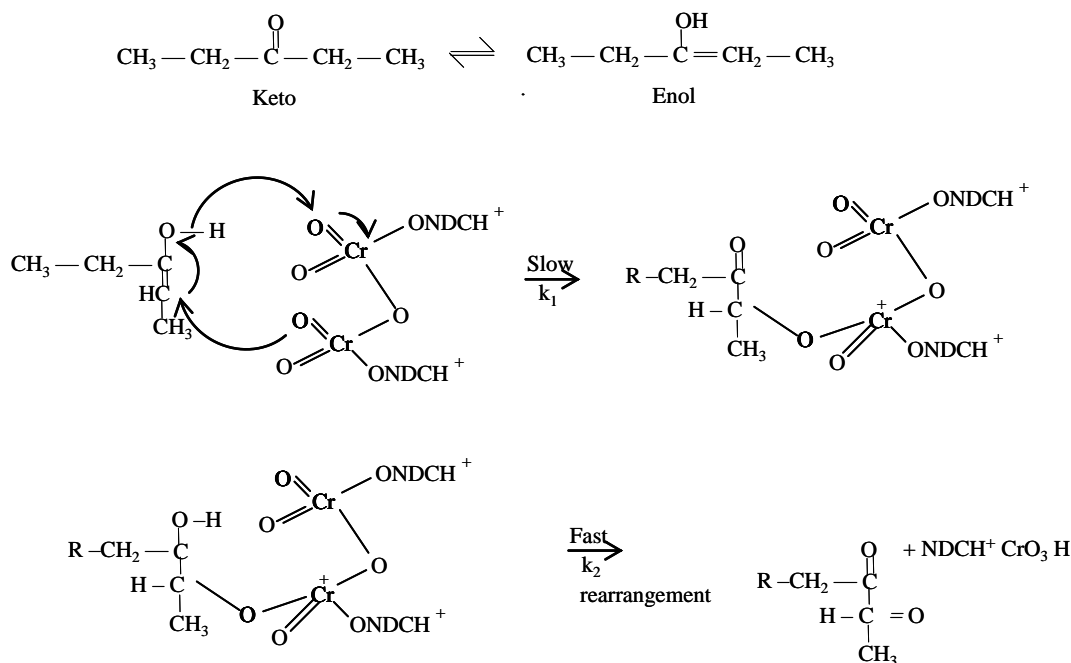
- (e) The addition of primary salt such as sodium chloride (NaCl), almost shows negligible salt effect on the reaction rate.
- (f) The addition of metal cation i.e. Cu⁺⁺ and Mn⁺⁺ ions to the system show variation in rates. The effect of increasing concentration of Cu⁺⁺ ions show an acceleration in the reaction velocity while Mn⁺⁺ ions retard the rate of oxidation.
- (g) The presence of free radicals in the system understudy was tested qualitatively by addition of 1-2 ml of acrylonitrile (monomer) in about 5-6 ml of the reaction mixture employing trapping method. The non-occurrence of turbidity and

white precipitate clearly indicate the absence of free-radicals in the system.

- (h) Corresponding diones were formed as the end-products of oxidation of 2-pentanone- NDC system which were identified by their melting points and also with existing conventional methods.
- (i) The stoichiometric determination have been found 1:1 mole ratio for substrate and oxidant (NDC).

Proposed mechanism for 2-pentanone -NDC system

The kinetic data as briefed in the beginning of the various sections of reveal that the reaction velocity follows nearly first-order kinetics at low concentration of 2-pentanone. Considering these facts a probable mechanism for the oxidation of 2-pentanone with NDC could be proposed as per following scheme :

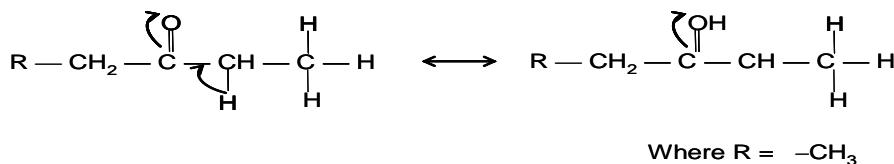


The rate expression leads the law

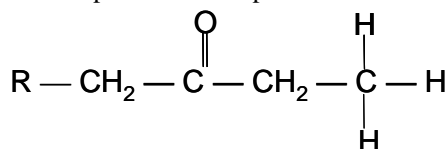
$$\frac{-d [\text{NDCH}^+]}{dt} = k_1 k_2 [\text{2-pent.}] [\text{NDC}] [\text{H}^+]$$

$$\frac{-d [\text{NDCH}^+]}{dt} = k_1 [\text{2-pent.}] [\text{NDC}] [\text{H}^+]$$

It is relatively more sterically hindered because of bigger $-C_2H_5$ group than $-CH_3$ group and thus increase in content of enol occurs due to exhibiting of probably tautomerism, consequently rate of reaction increase in 2-pentanone.

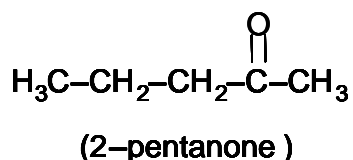


In pentanone, the $-CH_3$ group, with three hydrogen atoms is linked to the α -carbon atom in comparison to the other ketones with methylene group, with two hydrogen atom attached to the α -carbon atom. Therefore, 2-pentanone experiences greater tautomerism oscillation of protons in compared to the other 2-pentanone.



where $\text{R} = -\text{CH}_3$

The order of reactivity were found as :



The existed domainacy of steric, inductive and hyperconjugative effects among the molecules are the main reasons of above order of reactivity.

- (j) Various activation parameters namely temperature coefficient, energy of activation (E_a), frequency factor (A), enthalpy of activation (ΔH^\ddagger), free energy of activation (ΔG^\ddagger), and entropy of activation (ΔS^\ddagger) for each reaction have been calculated for 2-pentanone-NDC system. On the basis of experimental findings the reaction mechanism²⁴⁻²⁶, rate expression and order of reactivity have been discussed accordingly. The isokinetic plot has also been explained.

CONCLUSION

1. Kinetic studies employing NDC as an oxidant and allied aspects of its reactions lead us to conclude that the activity of NDC is much limited and needs to be explored in a broad way. It possesses vital potentiality and displays interesting behaviours at moderate condition of temperature.
2. Its use can be extended in analytical, applied chemistry and in separation/ identification of organic compound.
3. Fruitful outcome of the kinetic studies can suitably be applied in the field of pharmacology, Hi-tech, bio-chemistry, in finding the rate of growth¹⁹²⁻¹⁹⁷ of tissues and malignancy.

4. The study will certainly enlighten the future workers in carrying out researches of great value contribution and informations through kinetic study will enrich chemical literature to a great extent.
5. This work can better and suitably be utilized some branches of science to which kinetics is relevant are -

Branch	Application of kinetics
Biology	Physiological process (e.g. digestion and metabolism, bacterial growth, kinetics tissues, growth of malignancy).
Electrochemistry	Electrode processes pH, conductivity, transport phenomenon.
Geology	Flow processes
Organic chemistry	Reaction mechanism
Organic chemistry	Drug action, pharma co-dynamics
Physics	Viscosity, diffusion, nuclear processes

Colloidal and surface chemistry	Formation of electrical double layers
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