

Kintics and Mechanism Study on Oxidation of benzoin Catalysed by Selenium Dioxide

Dr. Mousa. Omran. Kadium

Dep. Of Chemistry, College Of Education for Women, University of kufa
Najaf-Iraq

الخلاصة

تمت دراسة حركية وميكانيكية اكسدة البنزين باستخدام ثاني اوكسيد السلينيوم في محيط حامض الخليك – ماء بنسبة ٦٠% (v/v) وقد وجد ان التفاعل من الدرجة الاولى بالنسبة الى كل من البنزوين وثاني اوكسيد السلينيوم كما تمت دراسة تأثير تركيز ايونات الهيدروجين على سرعة التفاعل بالنسبة بالبنزوين وقد لوحظ زيادة في سرعة التفاعل مع زيادة تركيز ايونات الهيدروجين وقد تم استخراج بعض الثوابت الحركية.

Abstract

The kinetic of oxidation of benzoin by selenium dioxid in 60% (v/ v) acetic acid water mixture have been investigated. The reactin is first-order with respect to both benzoin and selenium dioxide. The reactions are catalysed by strong acid: primary salt effect is studied. The reactions rate increases with increase in the concentration of benzoin and hydrogen ions concentration.

Introduction

Benzoin and benzoin derivatives are very efficient to photosensitizers for the free radical polymerization of unsaturated compound(1). Alsothey are used for various u.v polymerizabable system, protective coating photoresists and adhesives (2-4). Selenium dioxid has been used as oxidising agent in the kinetic study of oxidation of some ketones (5,6) similar saturated allylic alcohols are lacking although kinetics of oxidation of these with other oxidants (7,8) have been stuied. We now report the results of kinetics of oxidation of benzoin by selenium dioxd in acetic-acid mixture.

Experimental

All the chemicals used were of high purity of analytical grad, acetic acid (S.Merk) were used and selenium dioxide (BDH).

Selenium dioxide solution was prepared in distilled water and was standarised iodometrically. Aseries experiment were carried out varying values (t), reaction temperature (300-350) and benzoin concentrations(2-2.2×10M).

The product (benzil) was analyzed by heating the sampl with 0.5M potssium hydroxide solution, it is converted to the potassium salt of benzilic acid, which separated as a salt (9).

Selenium dioxide concentration (10 times) over benzoin at each experiment was used. unreacted selenium dioxide was determined iodometrically (10). The rate constants of each reaction were calculated by applying log (unreacted substrate) varies with time (min).

Results and discussion

Effect of benzoin concentration

The kinetic oxidation of benzoin has been studied when all the experiments were carried out under pseudo first order condition using ten fold excess of oxidant (SeO_2) over substrate (benzoin).

The variation in benzoin concentration was shown with the variation of the rate constants. The first-order rate constant were determined from (figure 1-5) and tabulated in Table (1).

The rate constants were increasing with increasing benzoin concentration, but the ratio of rate constants (k_s) over benzoin remain constant in Table (1).

Table 1: effect of benzoin concentration on the rate constants, temp. 300k

[SeO_2]=0.022 M, HOAC- water 60% (v/v)				
[benzoin] M	$K / 10^4 \text{ s}^{-1}$	$k/[\text{benzoin}]$	Unreact %	Time
2×10^{-3}	0.281	3.36	10	73
4×10^{-3}	0.33	3.57	12	67
8.2×10^{-3}	0.50	3.39	13	64.5
1.5×10^{-2}	0.67	3.44	16	57
2.2×10^{-2}	0.803	3.50	17	55

(unreact %), Time(min)

Effect of Selenium dioxide concentration

The variation in Selenium dioxide concentration shows that the reaction under study pseudo first-order in Selenium dioxide.

The rate constants of each reaction were calculated applying integrated first-order equation. The rate constants were determined with an accuracy ± 2 in kinetic. Table(2).

Table 2: Effect of SeO_2 concentration on reaction rate constants, Temp=300K

[Benzoin]=0.02M, HOAC-water 60% (v/v)		
[SeO_2] $\times 10$	$K/10^4\text{S}$	Time(min)
2.5	5.28	73
4	5.28	67
6.5	5.27	64
8	5.32	57
20	5.35	55

Effect of hydrogen ions concentration

The effect of hydrogen ion concentration on reaction rates has been studied by carrying the reaction in presence of varying concentration of perchloric acid, it is observed that the reaction rate increase with increasing concentration of perchloric acid increase, Table 3. Indicating the reactions are catalysed by acids, and from these results it appears that the dependence of rate on hydrogen ions concentration.

Table 3: Effect of hydrogen ion concentration on the reaction rate constants, at Temp.=300K with accuracy $\pm 2\%$

[Benzoin]=0.02M[SeO_2]=0.22M HOAC- water 60%	
[HClO_4]M	$K/10^4\text{s}^{-1}$
0.00	0.803
0.74	1.300
0.20	3.080
0.51	8.120
1.30	10.50

Effect of salt on reaction rate constants

The primary salt effect on reaction rate constant has been studied by adding aneutral salt (K_2SO_4) (0.00-0.24M). It is oserved that the primary salt effect is negligible (Table 4).

This fact suggest that at least one of the reactions involve in the rate determing step is a neutral molecule.

Table (4): Effect of Salt on the rate constants at Temp. 300 K, HOAC-Water=60/40(v/v)

[Benzoin]=0.02M, [SeO ₂]=0.222M, [HOCIO ₄]=0.	
K ₂ SO ₄ (M)	K×10 ⁴ S ⁻¹
0.000	0.803
0.100	0.821
0.250	0.820
0.400	0.880

Effect of temperature

The kinetics of oxidation of Benzoin have also studied and the values of the rate constants were estimated for each reaction temperature are give in Table(5). Since an increase in temperature increase in the rate constants. From arrehnius plot log k verus(1/T). The activation energy was calculated and found to be (16.8580 k.cal/mol).

Table (5): Effect of temperature the rate constants.

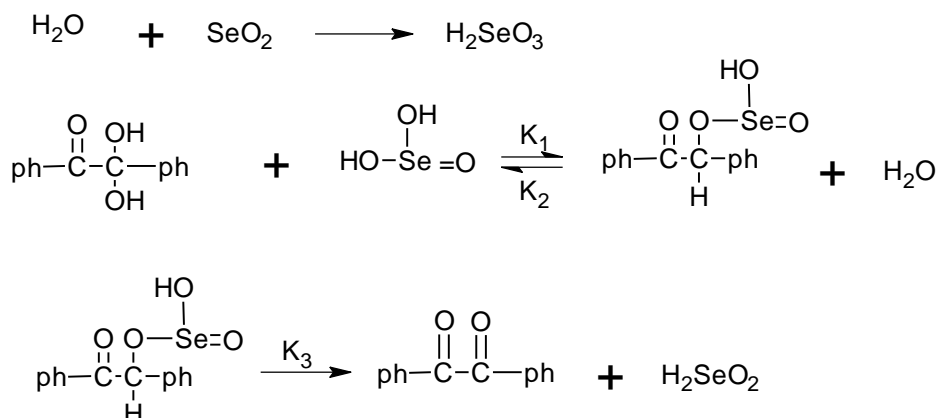
SeO ₂ = 0.22of, HOAC – Water 60%(v/v)		
Temp.C	1/T	K/10 ⁴ s ⁻¹
300	0.0033	0.803
320	0.0032	1.024
370	0.0027	1.380

Mechanism

It is reported that in the absenence of astrong acid the various species of selenium dioxide that the exist in aqueous acetic acid are HSeO₂⁺, H₂SeO₃ and ACH₂SeO₃(11,12) while in the presence of astrong acid, H₂SeO₂²⁺, H₃SeO₃⁺, and ACH₂SeO₃⁺ (11,12,13).

The mechanism of oxidation by selenium dioxide in aqueous acetic acid should be considere in term of H₃SeO₃⁺ or ACH₂SeO₃. the products of oxidation of Benzoin by Selenium dioxide are saturated ketones, which rules on the possibility of attack of oxidation species on the single bond of this compound to forms alkyl Selenite (I) which decomposed to a products .

The reaction passes through the following proposed mechanism



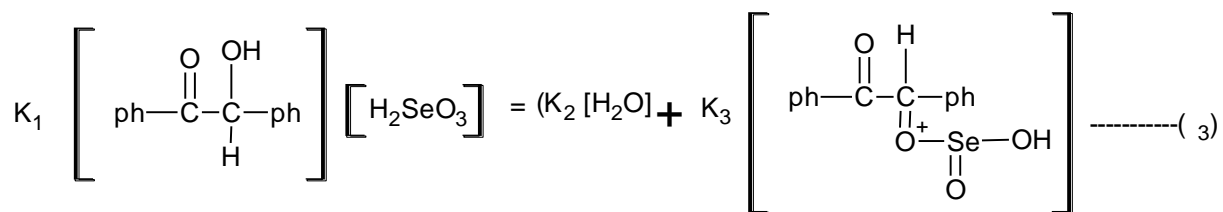
On the basic of the propsed mechanisum, the rate equation may be derived as follows, the rate at which product molecules are formed ;

$$\frac{d[\text{Product}]}{dt} = K_3 \left[\text{ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{O}-\overset{\text{HO}}{\text{Se}}=\text{O}}{\text{C}}-\text{ph} \right]$$

The rate at which Selenious acid react is.

$$\begin{aligned}
 \frac{d \left[\text{ph}-\overset{\text{O}}{\text{C}}=\overset{\text{O}^+-\overset{\text{OH}}{\text{Se}}=\text{O}}{\text{C}}-\text{ph} \right]}{dt} &= K_1 \left[\text{ph}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\text{C}}-\text{ph} \right] [\text{H}_2\text{SeO}_3] \\
 &- K_2 \left[\text{ph}-\overset{\text{O}}{\text{C}}=\overset{\text{H}}{\underset{\text{O}^+-\overset{\text{OH}}{\text{Se}}=\text{O}}{\text{C}}}-\text{ph} \right] [\text{H}_2\text{O}] \\
 &- K_3 \left[\text{ph}-\overset{\text{O}}{\text{C}}=\overset{\text{H}}{\underset{\text{O}^+-\overset{\text{OH}}{\text{Se}}=\text{O}}{\text{C}}}-\text{ph} \right] \text{-----} (2)
 \end{aligned}$$

At steady state, the equation (2) is equal zero



$$\left[\text{ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\underset{\text{O}^+-\text{Se}-\text{OH}}{\underset{\text{O}}{\parallel}}}{\text{C}}}-\text{ph} \right] = \frac{K_1 \left[\text{ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{ph} \right] [\text{H}_2\text{SeO}_3]}{(K_2 [\text{H}_2\text{O}] + K_3)} \text{-----} (4)$$

Substitution equation (4) in equation (1)

$$\frac{d[\text{product}]}{dt} = \frac{-d[\text{Benzoin}]}{dt} = K_3 \frac{K_1 \left[\text{ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{ph} \right] [\text{H}_2\text{SeO}_3]}{K_2 [\text{H}_2\text{O}] + K_3} \text{-----} (5)$$

Since $K_3 \gg K_2$, there for

$$\frac{-d[\text{Benzoin}]}{dt} = K_3 \frac{K_1 \left[\text{ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{ph} \right] [\text{H}_2\text{SeO}_3]}{K_2} \text{-----} (6)$$

$$\frac{-d[\text{Benzoin}]}{dt} = K_1 \left[\text{HP}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{OH}}{\underset{\text{H}}{\text{C}}}-\text{PH} \right] [\text{H}_2\text{SeO}_3] \text{-----} (7)$$

The derived rate equation explains the observe first- order kinetic in both the substrate and oxidant in absence of strong acid. Also the rate equation for acid catalysed action may be derived by considering (H_2SeO_3) the reactive oxidizing species.

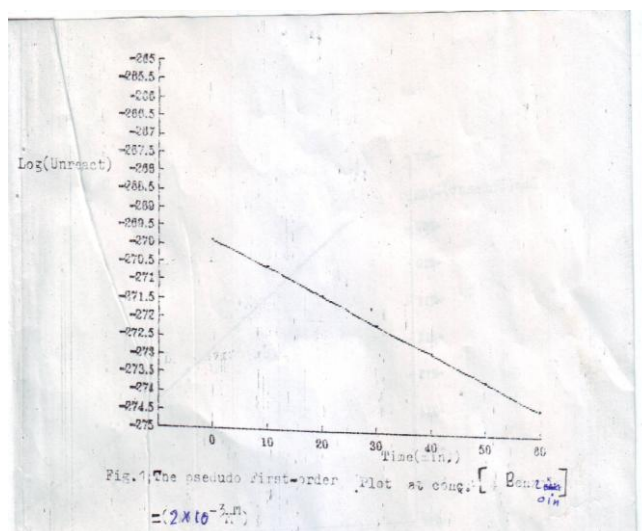


Fig. 1: The pseudo first-order plot at conc. [Benzoin] = $(2 \times 10^{-3} \text{ M})$.

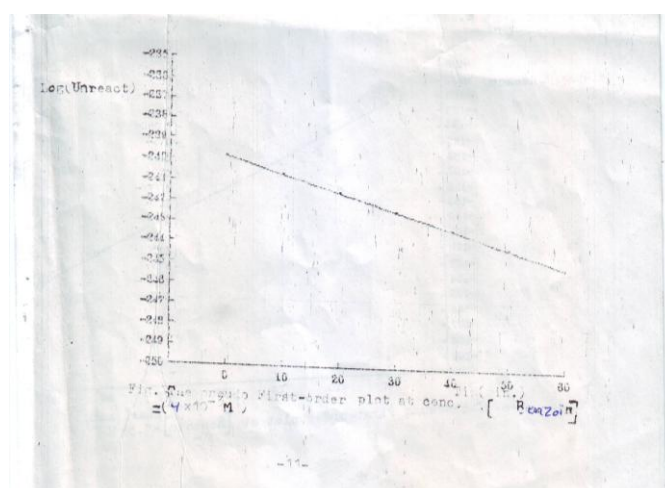


Fig. 2: The pseudo first-order plot at conc. [Benzoin] = $(4 \times 10^{-3} \text{ M})$.

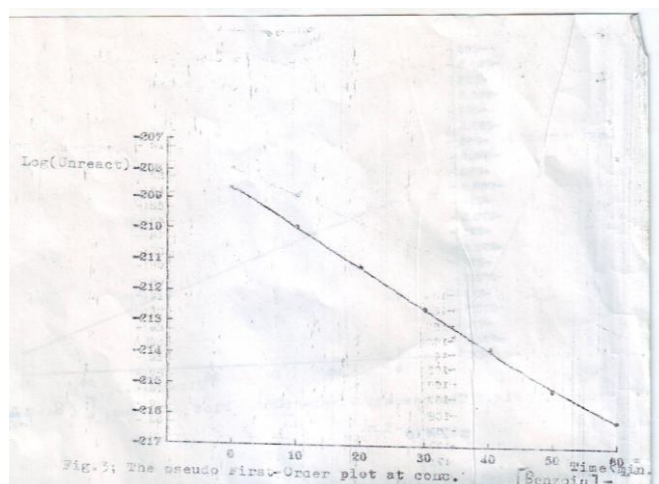


Fig. 3: The pseudo first-order plot at cono. [Benzoin] = $(8.2 \times 10^{-3} \text{M})$.

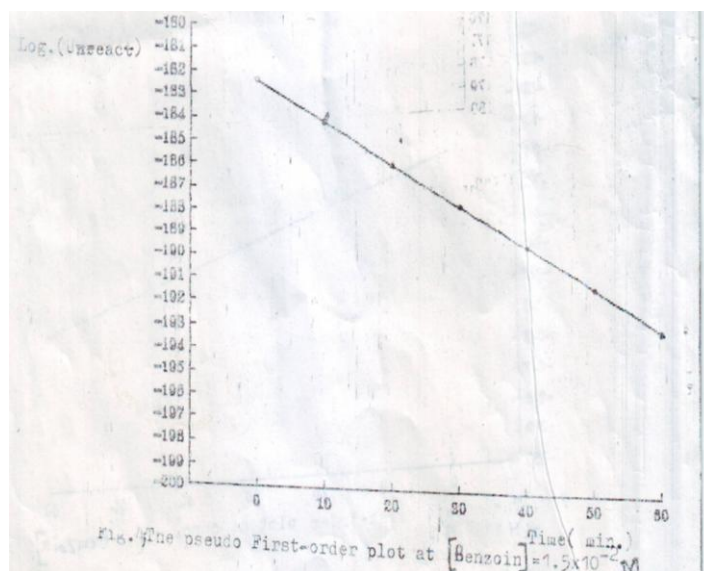


Fig. 4: The pseudo first-order plot at cono. [Benzoin] = $(1.5 \times 10^{-2} \text{M})$.

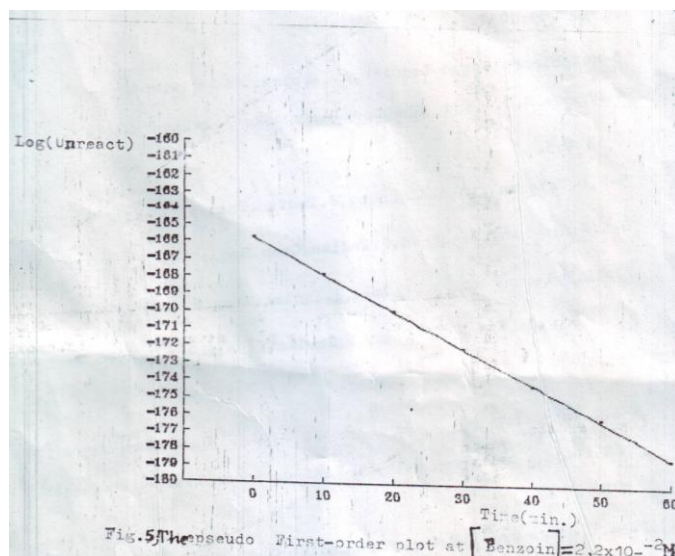


Fig. 5: The pseudo first-order plot at cono. at [Benzoin] = $(2.2 \times 10^{-2} \text{M})$.

References

- 1) R. Kuhlmann and W. Schuaole. Polymer, 1977, 18, 1163
- 2) H. G. Hein, Rosenkeanz H. J. and Rudolph, H. Angew. Chem., 1972, 84, 1032.
- 3) Hutchinson J, and ledwith A., polmer, 1973, 14, 405.
- 4) Pappas S. D., and Chattopadhyay A. K., J. Polemer Sci., 1975, 13, 483.
- 5) N. D. Valechn and A. K. Pandey, J. Indian. Chem. Soc. 1986, 670-673.
- 6) K. J. Singn and, S. Ananad, J. Indian. Chem. Soc., 1986, 61, 495.
- 7) N. D. Valechha and A. Pradhan, J. Indian. Chem. Soc. 1985, 24, 773.
- 8) D. S. Mahadava and H. M. Kmaiau, Indian. J. Chem, 4, 1976, 14, 808.
- 9) R. Q. Browster and William Organic Chemistry third Edition, Prentice-Hall of
- 10) India Private Limited New Delni 1971, 637.
- 10-K. J. Singh and S. H. Ananad, J. Indian Chem. Soc., 1979, 56, 363.
- 11)E. J. Corry and P. Scharver, J. Chem. Soc., 1960, 82, 918.
- 12) J. P. Schaefer, J. Am. Chem. Soc., 1962, 84, 713, 717.
- 13) J. P. Schaefer. B. Horvath and A. P. Klnin, J. Org. Chem., 1968, 33, 264.