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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Kinetic Studies on Darzens' Condensation of Chrysenequinone and its Mononitrogenous Derivatives

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

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SUMMARY

The kinetics of the following systems were followed potentiometrically, at different tempetaturesr in alkaline medium; (A) condens of chryseneqiuinone with phenacylychloride and with its p-methoxy, p-methyl and p-chloro derivatives. The condensation follow an overall third order kinetics, first with respect to each constituent.The rate increases by increasing the electron withdrawing power of the substituted groups. The rate also increases as the dielectric constant of the medium increases.(B)condensation of chrysenequinone, chrysenequinoneimine, and crhysenequinone monoxime with o-and p-nitrobenzy lchloeides. The reaction of the imine could not be followed because it was either partially hydrolyzed, or partially immiscible with the solvent. The condensations follow an overall second order kinetics, first with respect to the halogenmethylene compound and the alkali, and independent of the quinone. The rate of the reaction decrease as the dielcctric constant of the medium increases. The rate of condensation of chrysene quinone is faster than the monoxime. Also p-nitrobenzyl chloride reacts with chrysenequinonemuch faster than the o-derivative.

INTRODUCTION

We reported recently[1] on the base-catalyzed Darzens' condensation of phenanthrenequinone with substituted phenacyl chlorides. Since that study proved informative, we extended the investigation to different areas, concerning the quinone and the halogenomethylene compounds, to include (a) chrysenequinone with substituted phenacyl chlorides. (b) chrysenequinone with o- and p-nitrobenzyl chlorides. (c) chrysenequinoneimine and monoxime with the nitrobenzyl chlorides This choice was mainly to: (a) compare between chrysenequinone and phenanthrenequinone in their condensation with phenacyl chlorides. (b) compare between the different halogenomethylene compounds in their condensation with the same quinone. (c) investigate the effect of neighbouring groups on the reactivity of the adjacent carbonyl group in the quinone.

The kinetics of the condersations were followed up potentiometrically, in presence of sodium hydroxide, in aq. dioxane, at different temperatures.

EXPERIMENTAL

Materials: Chrysenequinone[2] (m.p. 239.5 °), chrysenequinoneimine[3] (m.p. 183 °), chrysenequinone monoxime[4] (m.p. 164 °), phenacyl chloride (m.p. 56–57 °), p-methoxy phenacyl chloride[5] (m.p. 98–99 °), p-methyl phenacyl chloride[6] (m.p. 56–57 °), p-chlorophenacyl chloride[7] (m.p. 101–102 °), p-nitrobenzyl chloride[8] (m.p. 72 °) and o-nitrobenzyl chloride (m.p. 48 °) of indicated purity were prepared or used, if available, as such. Peroxide-free dioxane[9] and doubly distilled water were used.

Kinetic measurements: The methods adopted for rate measurements were similar to those of Hine et al.[10], and Hanna et al[11]., involving potentiometric titration of the liberated halide ions, at different intervals, against $AgN0_3$ using Ag/AgCl-quinhydrone electrode. Carl Zeiss (Jena, D.D.R.) moving scale galvanometer was employed:

(A) The condensations of chrysenequinone with different substituted phenacyl chlorides were carried out in 60:40 and 70:30 (v:v) dioxaane: water mixtures, at 1 ° (for investigating the effect of the solvent). The runs in 70 % aq. dioxane were carried out also at 7, 10 and 15 ° to determine the thermodynamic activation parameters. The reaction was initiated by rapid addition of the quinone and the halogenomethylene compound in dioxane: water mixtures (previously cooled to the desired temperature) to the calculated concentration of the sodium hydroxide solution. At suitable time intervals, aliquots of the reaction mixture were pipetted out, quenched with 20 ml 0.1 N H_2S0_4, and analyzed for free halide ions.

Kinetic measurements could not be done below zero degree because the reaction mixture solidified.

(B) The condensation of chrysenequinone, chrysenequinoneimine and the monoxime with o– and p-nitrobezyl chlorides were carried out in 70: 30 dioxane: water mixture at 30 ° to determine the order of the reaction. The runs were carried out, in addition, at 15, 20, 25, 35 and 40° to determine the thermodybnamic activation parameters.

In all runs, the reactions were followed up to 75 % completion. Each run was repeated 3 times to check reproducibility. Isolation of of products: (A) In the condensation of chrysenequinone with substituted phenacyl chlorides, the constituents were dissolved in 1 liter of 70 % aq. dioxane, previously cooled to 1° in an ultrathermostat (type EIN, Germany, -20° to + 50 °C.) for two hours, then at room temperature overinght. Crystalline solides were separated after slow evaporation of the solvent at room temperature, washed with water and crystallized from the suitable solvent. Table 1 includes the different products obtained.

(B) For the condensation of the quinone and its monoxime with the nitrobenzyl chlorides, the method used for isolation of products was similar to that followed in (A), except that the addition was made at room temperature, and left for two days.

RESULTS AND DISCUSSION

Kinetics: (A) To permit accureta and reliable determinations of the rates for the condensations of chrysenequinone with the substituted phenacyl chlorides, the used molar concentrations of the reactants were 0.001: 0.001: 0.01 M of chrysenequinone 'A': phenacyl chloride (or its substituent) ,B': sodium hydroxide, respectively. Higher concentrations led to very fast reactoins that could not be followed. The kinetic results showed that the condensation reaction is an overall third order, first with respect to each constituent. (Table 2) includes the rate constants obtained for different molar ratios employed. Fig. 1 shows the graphical representation of pseudo-second order kinetics using excess sodium hydroxide (1:1:10). Fig. 2 shows true third order representation when equimolar initial concentrations were used.

(B) In the condensation of the quinone and its monoxime with 0 – and p-nitrobenzyl chlorides, the molar concentrations used were 0.005: 0.005: 0.05 M of the quinone ,A': nitrobenzyl chloride ,B': sodium hydroxide, respectively The kinetic results showed that the condensation reaction is an overall second order, first with respect to nitrobenzyl chloride and the alkali, and independent of the quinone.

Table (1)

Products from Darzens' reaction of Phenanthrenequinone with p-substituted Phenacyl chlorides in alkaline medium.

Compound (I)	Formula	Yield %	m.p. °C.	Found			Required			νmax cm⁻¹		Solvent of
				C	H	Cl	C	H	Cl	νmax 0H	νmax C=0	crystallization
X = H	$C_{12}H_{14}0_3$	94.4	197.8	80.5	4.3	–	81.0	4.3	–	3326	1695	2 : 1 gl. acetic: H_10(v/v)
X = Cl+	$C_{22}H_{13}0_3Cl$ (keto form)	50.0	165	73.0	3.8	9.7	73.2	3.6	9.8	–	1680	methanol
X = Cl	$C_{22}H_{13}0_3Cl$	95.5	210	72.9	3.3	9.9	73.2	3.6	9.8	3320	1695	methanol
X = CH_3	$C_{23}H_{16}0_4$	91.8	176	81.0	5.0	–	81.2	4.7	–	3230	1700	benzene-pet. ether (40–60)
X = OCH_3	$C_{23}H_{16}0_3$	89.9	184	77.7	4.4	–	77.5	4.5	–	3230	1700	benzene-pet. ether (40–60)

+ This compound was obtained when the reaction was carried out at –3° with molar ratio of 1:1:1 of A: B: OH^- components, respectively; along with 40 % enol form. (Initial concentration of phenanthrenequinone 0.001 M)

Table 2

Rate constants for condensation reactions of chrysenequinone with phenacyl chlorides at 1°, in 70 % aq. dioxane.

substituted phenacyl chloride (0.001 M)	molar ratio of A: B: $0H^-$		
	1: 1: 1	1: 1: 10	1: 1: 10
	k_3 l^2/mole^2. sec	k_2 l/mole. sec	k_3 l^2/mole^2. sec
p-chloro	4.44×10^2	20.8	20.8×10^2
unsubstituted	2.78×10^2	13.33	13.33×10^2
p-methyl	1.85×10^2	8.33	8.33×10^2
p-methoxy	1.39×10^2	5.91	5.91×10^2

The oxime was found to be more stable in 70 % aq. dioxane than the corresponding imine, since the product isolated was purely nitrophenyl chrysoxazolr[12]. This result was confirmed previously[13], that the oxime is more stable towards hydrolysis than the imine.

Figs. 3 & 4 show pseudo-first order representation when excess alkali is used (1:1:10) whereas Figs. 5&6 show true second order repreientation when equimolar initial concentrations were used. Solvent effect: (A) It was found that the rate of condensation of chrysenequinone with phenacyl chloride or its substituents, increases as the dielectric constant of the solvent increases. In 50 % aq. dioxane the quinone precipitated at zero time of the reaction, and in 80 % aq. dioxane the reaction mixture began to solidify at 1° during kinetic measurements. Hence, only 60 % and 70 % aq. dioxane mixtures were studied.

(B) In the condensation of the quinone, or its monoxime, with 0 – and p-nitrobenzyl chlorides, only two mixtures of aq. dioxane could be investigated, which are the 65:35, and 70:30 (v:v), dioxane: water; due to the difficult solubility of the quinone. It was found that the rate constant of the reaction increases as the dielectric constant of the medium decreases. In 60 % aq. dioxane, the quinone precipitated at zero time of addition, whereas in 80 % aq. dioxane partial miscibility of sodium hydroxide took place. Effect of Substituents: (A) It was found that electron withdrawinh substitueuts increase the rate of condensation of chrysenequinone with pheneacyl chloride, while electron repelling substituents decrease that rater This shows that the order of accelarating the rate is: $Cl > H > CH_3 > OCH_3$. This result is also substantiated by the linear relation of σ vs. log k/k_0, showing the validity of the Hammett equation (Fig. 7). A positive value of ρ shows that the reaction is enhanced by withdrawal of elecron density from the reaction center, and vice vera. Table 3 includes thermodynamic activation parameters calculated from the temperature dependence of the rate constants.

Table 3
Thermodynamic activation parameters for condensation of chrysenequinone with phenacyl chlorides.

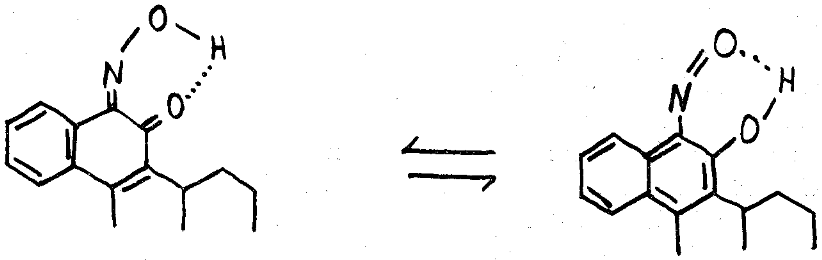
substituted phenacyl chloride	E* K. cal/mole	$\triangle H^*$ K. cal	$\triangle S^*$ e.u.	$\triangle G^*_{274}$ K. cal.
p- chloro	7.77	7.23	-33.77	16.48
unsubstituted	8.67	8.13	-31.35	16.72
p-methyl	9.15	8.61	-30.54	16.98
p-methoxy	10.07	9.52	-27.88	17.16

(B) For the condensation of chrysenequinone and its monoxime with o- and p-nitrobenzyl chlorides, it was found that p-nitrobenzyl chloride reacts faster than the o-derivative. This is attributed to both steric and electronic effects caused by the nitro group in the ortho position to the carbanion carbon.

On studying the effect of suastituents on the reactivity of the adjacent carbonyl group in the quinone, it was found that the rate of reactions is in the order.

chrysenequinone > oxime

This result could be explained by assuming the formation of an intramolecular hydrogen bond, whose formation was proved to take place in o-quinone monoxime,[14] where it changes easily to the corresponding 1-nitroso-2-ol, as follows:



Tables 4 and 5 include the thermodynamic activation parameters for these condensations.

Table 4

Thermodynamic activation parameters for condensation of chrysenequinone with nitrobenzyl chlorides.

halogeno methyene compound	E^* K. cal/mole	$\triangle H^*$ K. cal	$\triangle S^*$ e.u.	$\triangle G^*_{303}$ K. cal
o-nitrobenzyl chloride	15.4	14.798	-19.481	20.701
p-nitrobenzyl chloride	14.3	13.698	-21.689	20.270

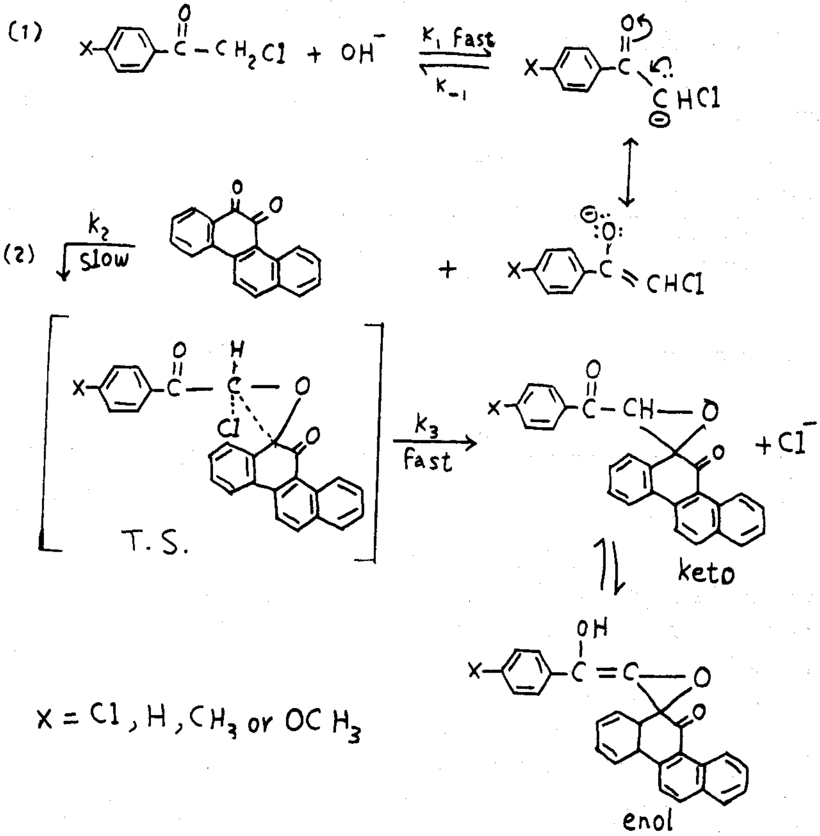
Table 5

Thermodynamic activation parameters for condensation of chrysenequinone monoxime with nitrobezyl chlorides.

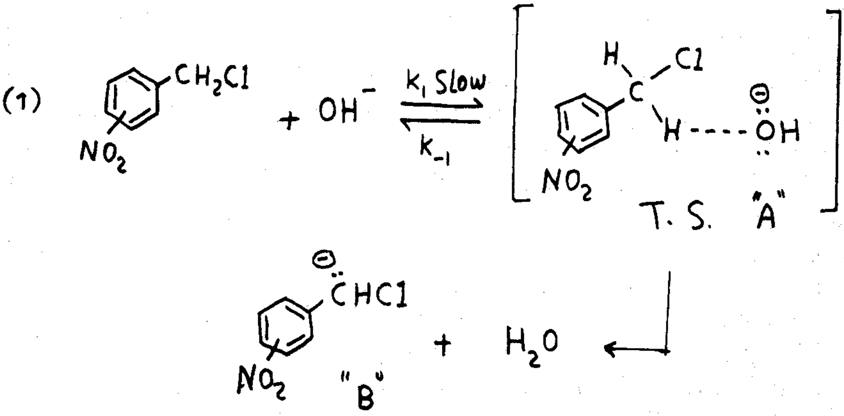
halogeno methylene compound	E^* K. cal/mole	$\triangle H^*$ K. cal	$\triangle S^*$ e.u.	$\triangle G^*_{303}$ K. cal
o-nitrobenzyl chloride	17.6	16.56	-17.76	21.94
p-nitrobenzyl chloride	16.02	15.41	-18.85	21.12

Mechanism: (A) It is clear that the condensations of chrysenequinone with phenacyl chloride and its substituents, follow the same path of results that we reported earlier[1] for phenanthrenequinone with the same phenacyl chlorides, which substantiates our previous conclusions[1]. The results show, however, that chrysenequinone enhances the condensations more than phenanthrequinone. Accordingly, we can propose the following mechanism that we proposed before. and which is similar to that proposed by Ballester[15]: Since the reaction was found to be third order, hence, step (2) is considered to be the rate limiting step. It can be seen that the formation of the product in step (1) is favoured by electron withdrawal in the indicated direction, thus facilitating the removal of the H^+ by the $0H^-$ group, and stabilizing the developed negative charge. This should explain the order of rate acceleration of the different substituents that we reported.

(B) The second order kinetics for the condensation of chrysene quinone or its monoxime with the nitrobenzyl chloride can be explained according to the following mechanism: In step (1) the base slowly abstracts an α - proton from the nitrobenzyl chloride to form the carbanion «B". This slowest step is the rate-limiting step. The presence of the highly electron-withdrawing nitro group facilitates the abstraction of the α - proton, since it decreases the electron density on the methylene-carbon. step (1) is reversible with $k_1 >> k_{-1}$.

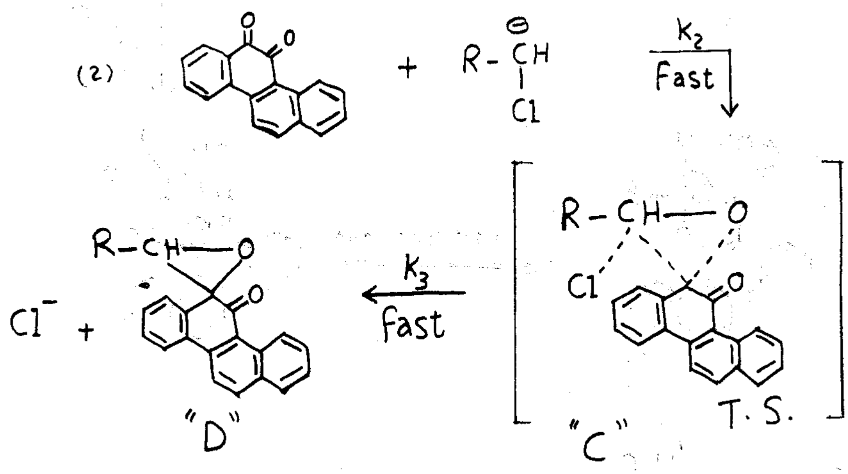


X = Cl, H, CH_3 or OCH_3



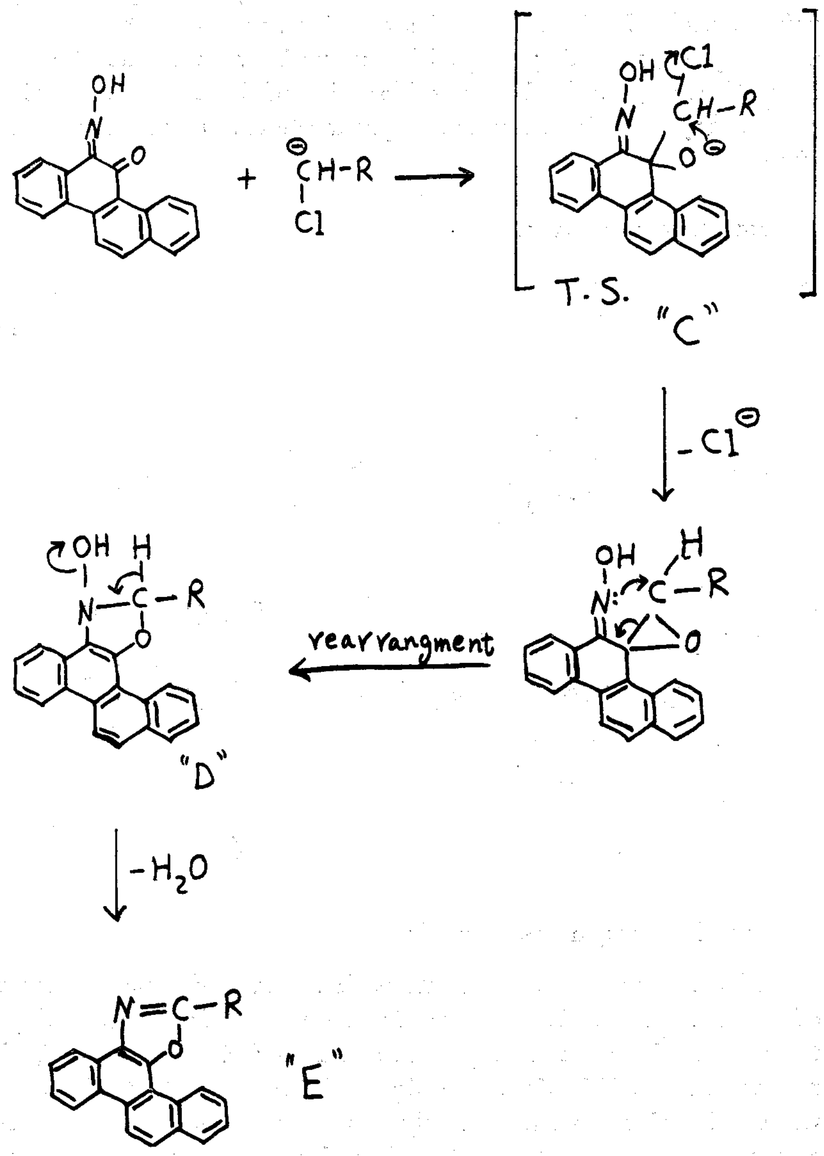
As fast as the carbanions are generated, they are trapped up by the quinone molecules in the second step (2), where the carbanion acts as a nucleophile, attacking the positive center in the quinone. This step is faster than (1), and leads to the formation of the keto epoxide «D” in case of chrysenequinone, or the chrysoxazole «E” in case of the monoxime:

for chrysenequinone:



for chrysenequinone monoxime[12]:

The decrease of reaction rate with increase of dielectric constant of the medium, i.e. with increase of water content, is most probably due to the hydration of the highly polar nitrobenzyl chloride ion «B”, which results in its stabilization. The higher the water content, the stronger the stabilization. and accordingly the greater the amount of energy required to decompose the hydrated species, which means a slower reaction rate. The same conclusion was established before by Hanna et al[11].



R = $C_6H_4-NO_2$ (p-) or $C_6H_4-NO_2$ (o-)

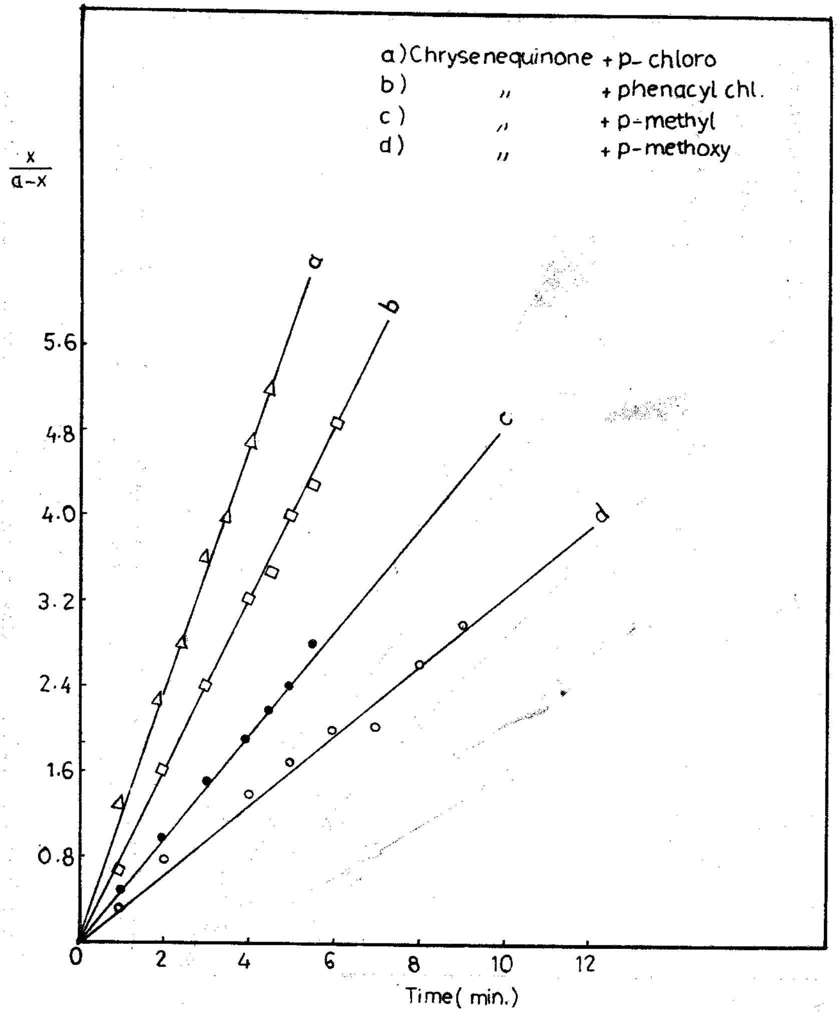


Fig. 1 Pseudo-second order kinetics for chrysenequinone with phenacyl chloride and its substituents. Molar ratios 1:1:10.

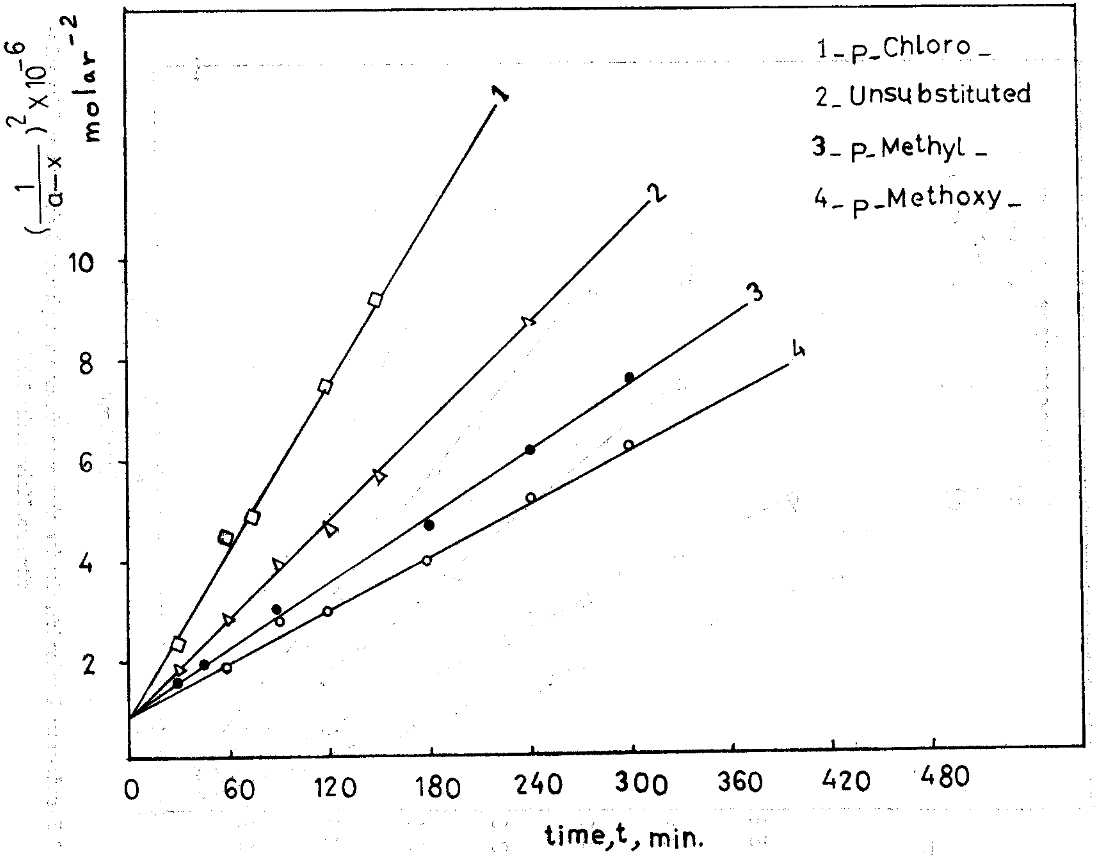


Fig. 2 True third order kinetics for chrysenequinone with phenacyl chloride and its substituents.
Molar ratios 1:1:1.

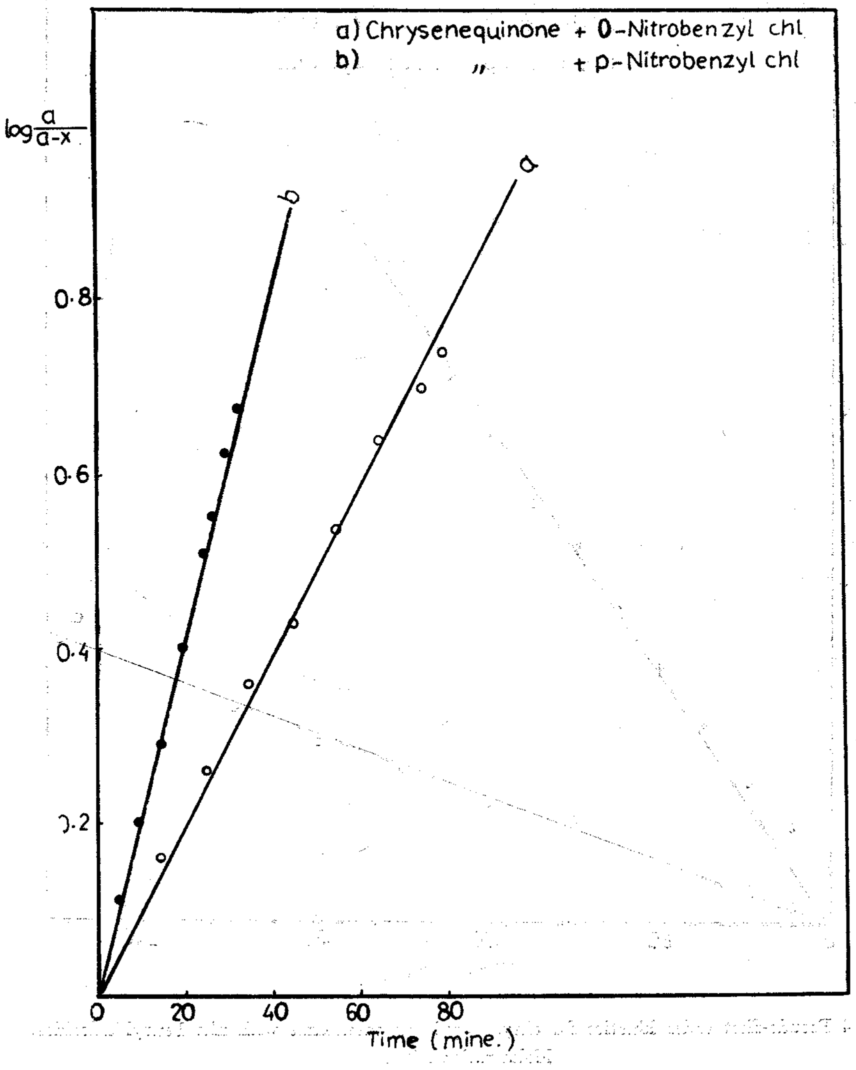


Fig. 3 Pseudo-first order kinetics for chrysenequinone with nitrobenzyl chlorides. Molar ratios 1:1:10.

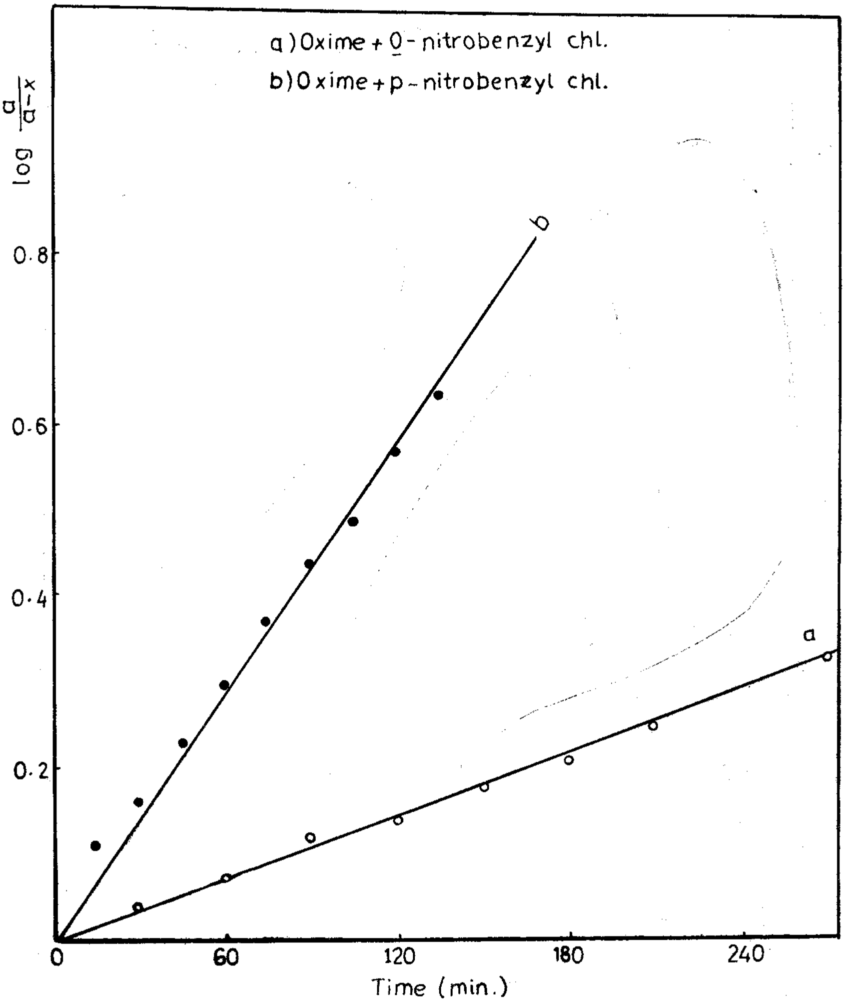


Fig. 4 Pseudo-first order kinetics for chrysenequinone monoxime with nitrobenzyl chlorides. Molar ratios 1:1:10.

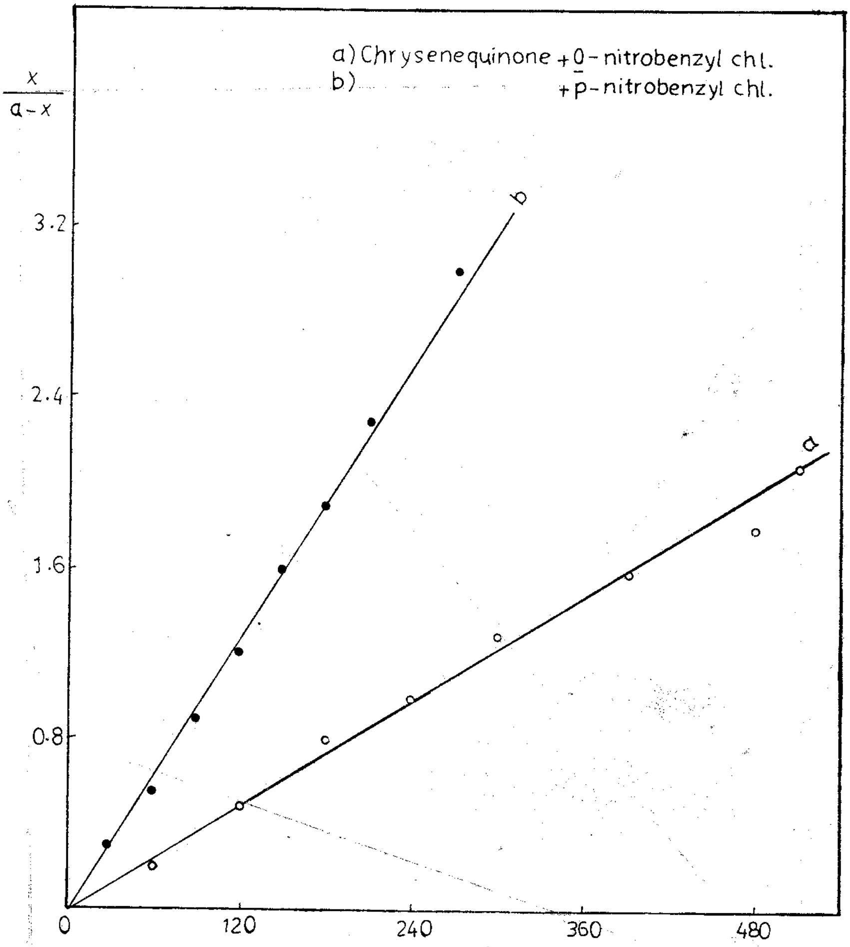


Fig. 5 True second order kinetics for chrysenequinone with nitrobenzyl chlorides. Molar ratios 1:1:1.

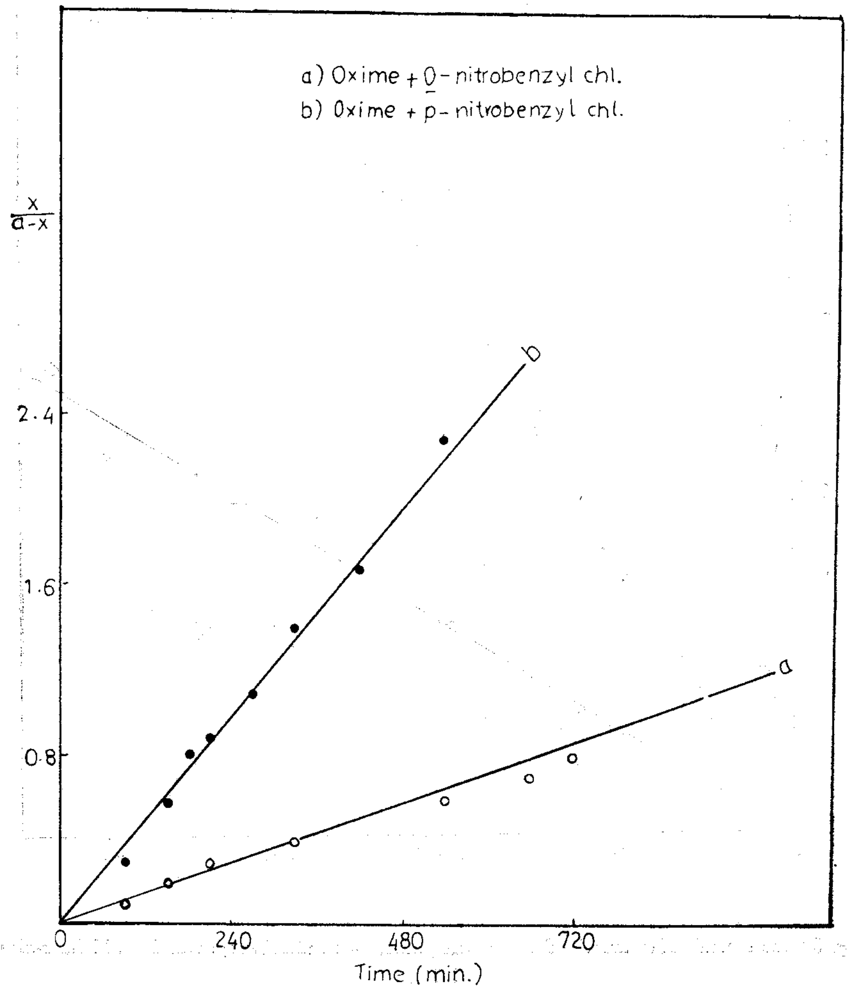


Fig. 6 True second order kinetics for chrysenequinone monoxime with nitrobenzyl chlorides. Molar ratios 1:1:1.

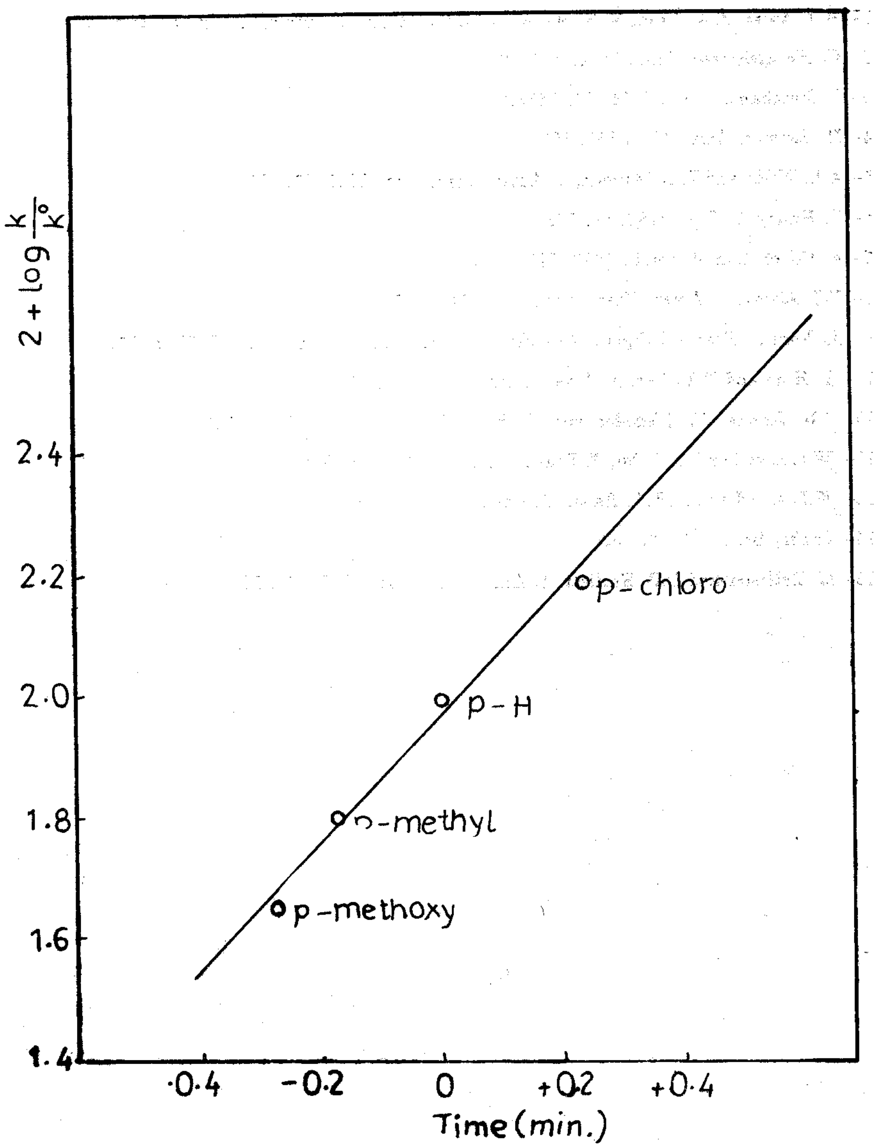


Fig. 7 Validity of Hammett equation for chrysenequinone with phenacyl chloride and its substituents.

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