KINETICS AND MECHANISTIC STUDIES OF THE BROMINATION OF SOME SUBSTITUTED TETRALONES, PART 1

By
Abdul Majeed M. Dabbagh* Mikdad T. Ayoub**
*Dept. of Chemistry, College of Science, Mosul University, Iraq
**Department of Chemistry, College of Science[1]
Hashemite University, Zarka, Jordan

دراسات ميكانيكية وحركية لمعدلات البروم في بعض المواد

عبد المجيد الدباغ

قسم الكيمياء – كلية العلوم – جامعة الموصل

الموصل – العراق

مقداد أيوب

قسم الكيمياء – كلية العلوم – الجامعة الهاشمية

الزرقاء – الأردن

في هذا البحث تم قياس معدلات سرعة تفاعلات البروم مع ٢– بنزال –١– تترالون (I1) وكل من مشتقاته بارامثيل (I2)، بباراكلورو (I3)، ميتاكلورو(I4) وبارانايترو(I5)في الكلوروفورم كوسط للتفاعل، وقد دلت الدراسة على أن جميع التفاعلات ذات حركية من الرتبة الأولى لكل من البروم والمواد المتفاعلة معه، ويتباين معدل السرعة وفقاً للتسلسل   I2 < I1 < I3 < I4 < I5 عند أية درجة حرارية مما يشير على أن التفاعل يتأثر بالحث والعوامل الالكترونية الأخرى التي تسببها المعوضات المختلفة وأن هذه العوامل تلعب دوراً مهماً باستقرارية المركبات الوسطية، وقد تم اقتراح ميكانيكية منسجمة مع النتائج العملية وإشتقاق معادلات سرعة متفقة مع هذه الميكانيكية.

ABSTRACT

The rate of bromination of 2-benzal-1-tetralone (I1) and its derivatives *p*-methyl (I2), *p*-chloro (I3), *m*-chloro (I4), and *p*-nitro (I5) have been studied in chloroform. The study indicated first order dependence on each of reactants with rates I2 > I1 > I3 > I4 > I5 at any temperature. The effect of substituents on the rate showed that electronic factors, inductive and conjugative effects play reasonable role on the stability of the intermediates. Suggested mechanisms, which are consistent with the results have been postulated and suitable rate laws in consonance with the suggested mechanisms have been derived.

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* Address for correspondence.

[1] Present address: Hashemite University, Zarka, Jordan; College of Science, Department of Chemistry.

INTRODUCTION

α, β Unsaturated ketones and their brominated analogues are considered to be very important for human life. Some of these compounds, have a biological activity as antibacterial (Muftic, 1971; Laliberte et al., 1967; Albercht et al.; 1971), others are useful for industry (Max et al., 1971; Rosenkranz et al., 1970).

Although the exothermic addition of bromine to olefines has been studied extensively for many years (Freeman, 1975), mechanistic studies on the bromination of exocyclic α, β unsaturated ketones such as tetralones (Rout et al., 1970; Mohapatra et al., 1972) have not yet been studied, and still remained some what obscure.

Here we report a first complete kinetic study on the bromination of exocyclic α, β-unsaturated ketones e.g. substituted 2-(phenylmethylene)-3,4-dihydro-1 (2H)napththalenones, (2-benzal-1-tetralones), I to the corresponding dibromides II, in chloroform.

Mechanisms of the reaction process were proposed to explain the experimental observed rate laws and products formed with the aim of analysing the influence of substituents (x) in the phenyl ring on the stability of the expected transition state and intermediate.

EXPERIMENTAL

Materials :

The bromine used was of analar grade as supplied by Fluka Company. The chloroform, (BDH), was purified by washing with (2N) NaOH, concentrated H_2SO_4 and water, dried over K_2CO_3, distilled and immediately used. All tetralones were prepared in the department by standard procedure (Al-Iraqi, 1998). All organic compounds used for the syntheses were commercially available and purified before use.

Kinetic Measurements :

Kinetics were followed by u.v. spectrophotometry on a Shimadzu Spectrophtometer, monitoring the disappearance of bromine at a fixed wave length (407-427 nm).

Stock solutions of substituted tetralone I(1-5) in chloroform were prepared, $(4.5 \times 10^{-2}$ M), 2 mL of this solution was transferred to a u.v. cell at the appropriate temperature, 1 mL of $09. \times 10^{-2}$ M bromine in chloroform was added to start the kinetic run. A reference cell containing 2 mL of tetralone

compund and 1 mL chloroform was always used. The instrument was programmed to take readings at different intervals. All kinetic runs were carried out, at least, in duplicate.

RESULTS AND DISCUSSION

Preliminary experiments showed that reasonable rates of Bromination were obtained at a temperature range between 283-303K. No compounds other than I and II were ever detected in the product of these reactions as shown by their u.v. analyses under kinetic conditions; TLC which showed a unique spot as the only product and finally the CHN mirco analyses confirm this. Typical runs of reaction toward completion demonstrate very clearly how the absorbance of Br_2 at infinite time. A_{∞}, does not change its value and position when the temperature is changed indicating that the reaction is completely forward and no equilibrium between reactants and products is ever existed. These observations suggest that the addition reaction proceeds clearly according to the simple stoichiometry of the raction:

whence X   1   2   3   4   5

       H   p-CH₃   p-Cl   m-Cl   p-NO₂
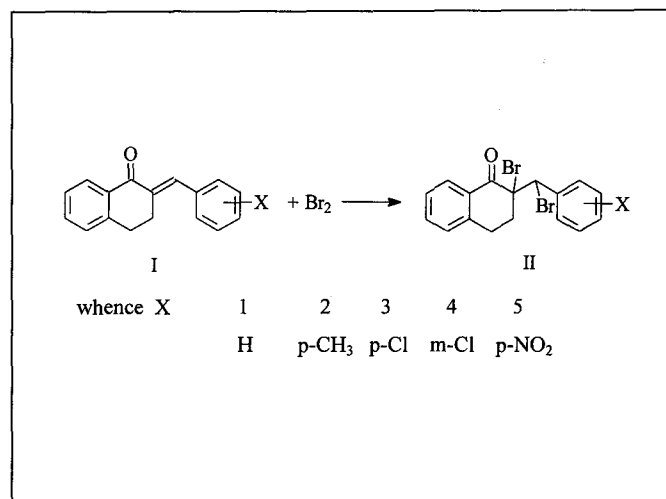
Since tetralones I (1-5) were used in large quantities compared to bromine (10 mole ratio), the results were analysed as a pseudo-first order reaction for which the differential rate equation (r) is:

$$r = k_{obs} [Br_2] \quad \text{...} (1)$$

where kobs represents the observed rate constant and is a function of tetralone concentrationi i.e. $k_{obs} = k$ [Tetralone]. The change in the absorbance of the bromine at (407-427 nm) with time was followed, since an intense band was observed at this region, which is not interfered with any other peak of the reaction mixture. Therefore, integration of equation (1) taking the bromine analyses into account leads to the integrated form (2):

$$Ln\left(\frac{A_0 - A_\infty}{A_0 - A_t}\right) = k_{obs}t \quad \dots\dots\dots\dots\dots\dots\dots\dots (2)$$

where A referes to the absorbance of the bromine and the subscript o refers to t = 0. Excellent straight lines were obtained with zero intercepts when equation (2) is performed with slopes corresponding to the obsered rate constant, k_{obs} such plots showed very good agreement between repeated runs and were linear for as long as followed (less than two half lives), confirming the pseudo-first order kinetics and proving a 1st order kinetics with respect to bromine. At a range of temperatures between 10 – 30°C, runs were carried out for reactants at constant concentrations, the observed rate constants were calculated from the slopes of the plots as shown in Table 1. The standard error σ of the slope of a plot, shown in table 1, simply represents the uncertainty due to the scatter of the point about the regression line, and is thus a measure of the reproductibility of the results rather than its absolute accuracy. Typical plots for the ractants I (1-5) at 25°C are exhibited in Figure 1. On the other hand, tests were made for the order of the reactants I (1-5). Kinetic runs, at different concentrations of I (1-5) were performed. Linear plots were obtained when the functions of Log Kobs vs Log [Tetralone] were demonstrated with slopes of unity proving, according to equation (3), a first order kinetics with respect to tetralones I (1-5).

$$Log k_{obs} = Log k + nLog[Tetralone] \quad \dots\dots\dots\dots\dots (3)$$

Hence a total second order kinetics was confirmed.

Arrhenius plots of Ln k_{obs} vs the reciprocal of the absolute temperature over a temprature range of 20°C were performed. The plots were excellent straight lines as shown in Fig. (2). Arrheinus paramters and entropies of activation are tabulated in Table 2.

Activation Parameters :

The value of the activation paramaters (Table 2) is of great importance to discern the mechanisms under all circumstances of the tudy (Dabbagh, 1996). The energies of activation, for I (1-5), are generally similar in value with those of olefinic bromination (Bamford et al., 1973) and vary within 77-91 kJ.mol^{-1}. The variation in their values may be attributed to electronic factors supported by the substituent groups (X). It is expected that electron donating substituents enhance the electrophilic reaction, whereas electron withdrawing substituents retard it (Dabagh, 1996; Bamford et. al.,

1970). These factors, as well as, the combined inductive and conjugative effects of the substituents (X) result in differences in rates according to the following order:

p-CH$_3$ > H > p-Cl > m-Cl > p-NO$_2$

At first sight, the reaction may occur by initial π-interaction of the C=C double bond in I with the electrophilic bromine to form a stabilized charge transfer complex. The electron donating substituents at phenyl ring, such as p-ch$_3$, play important role in stabilizing this complex leading to the formation of a bromonium ion, thus enhances the reaction rate (Table 1) as compared with the corresponding hydrogen analogue.

Such a fast reaction is supported by its low activation energy

Scheme I
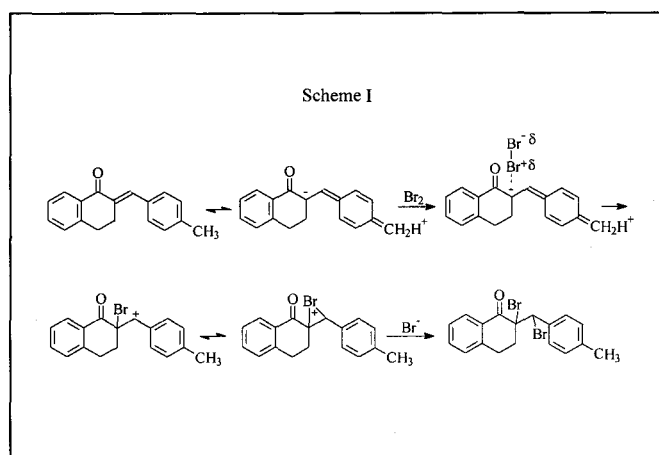
(Table 2). This value is fairly reasonable for reactions having highly polar transition state (Atkinson and Bell, 1963).

In contrast, electron-withdrawing groups such as p-Cl, m-Cl, p-NO$_2$ result in regular decrease of bromination rates, as compared with the corresponding hydrogen analogue according to the following sequence:

H > p-Cl > m-Cl > p-NO$_2$, Since they destabilized the charge transfer complex, thus retard the reaction rate; hence a higher activation energy is required (Table 2). The relatively low values of k_{obs} for NO$_2$ is, thus, attributed to the high electron density at the reaction center, i.e. the C=C double bond, and subsequently reduces the possibility of the formation of the charge transfer complex; thus a higher activation energy is required to form the intermediate bromonium ion.

The chloro group, on the other hand, possess a lower electron withdrawing ability than the nitro group (March, 1968). Hence its ability to retard the bromination process is less than the nitro group, as shown in Table 1. Also the p-chloro reactants are more reactive than m-chloro ones. The chloro group exhibits two types of electronic effects, reso-
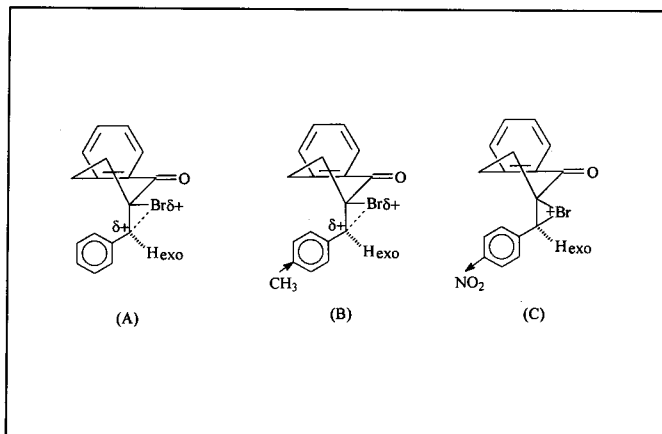
nance and predominant inductive effects (Marcy, 1968). The later applies to both *meta* and *para* positions.

The entropies of activation $\Delta S^{\#}$, which are tabulated in Table 2 are all largely negative values, and this is in strong agreement with the involvement of a considerably three membered rigid bromonium ion intermediate with less freedom of internal motion than reactants themselves (Yates and Wright, 1976; Freeman, 1975; Dabbagh and Al-Hamadany 1987; Dabbagh 1996). Again, it can be clearly discerned the effect of electronic properties of the different substituents on the cyclic intermediate by noting the differences in $\Delta S^{\#}$ value for the methyl I(2) is much lower than others due to the increase of electron density at the reaction center leading to the formation of a highly oriented stable bromonium ion. In contrast, the highest $\Delta S^{\#}$ value for the nitro I(5) may be attributed to a decrease in electron density which, in turn destabilizes the intermediate. Therefore, it becomes clear that the intermediate is a three membered ring, which is strongly rigid bromonium ion.

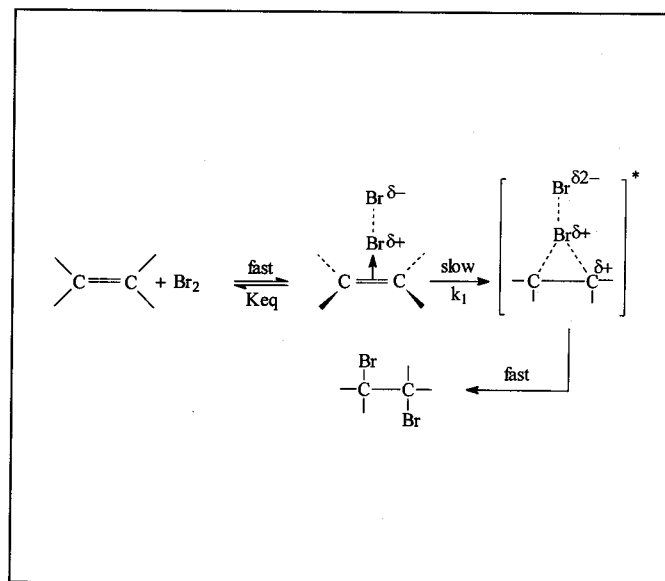This bromonium ion may be symmetrical or asymmetri-

cal in shape depending on the structure of the reactant (Rolston and Yates, 1969; Yates nd McDonald, 1973). The asymetrical bromonium ion is more realistic for the bromination of chalcones (Yates and McDonald, 1973). Therefore, it expected that the pargially positive charge lie on the carbon, away from the carbonyl group (A). The intensity of the partially positive charge on the β-carbon depends on the substituent at the phenyl group.

In case of *p*-methyl compounds, it is believed that a favoured tightly rigid asymmetrical bromonium ion (B) with a very low negative value of $\Delta S^{\#}$ is formed. While in the case of nitro compounds, the structure is tightly symmetrical

bridged bromonium ion (C) with a fairly low negative value of $\Delta S^{\#}$.

Rate Equation:

It is implied that a rapid preequilibrium formation of a 1:1 transitory charge transfer complex between tetralone I (1-5) and bromine. Presumably this complex may lead by a slow step to the formation of a bromonium ion. Subsequent ring open of the bromonium ion would then lead, by a fast step to observed products.

This fact is confirmed by the second order rate equation
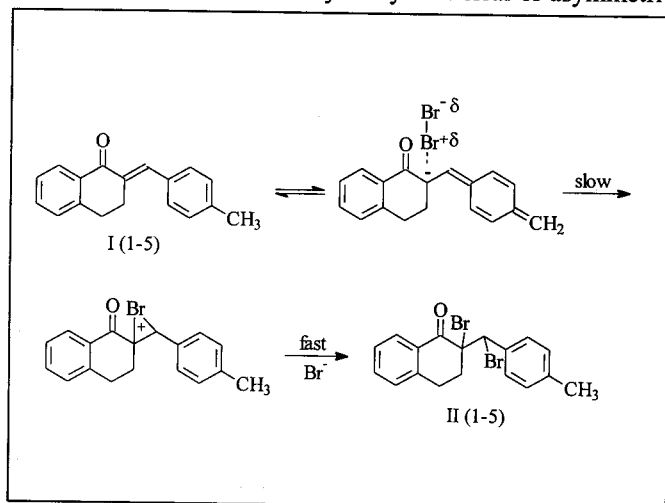

with unit order to each of te reactants.

$$r = k \, [\text{Tetralone}] \, [\text{Bromine}] \quad\quad\quad (4)$$

where $k = K_{eq}k_1$; and also by the pseudo first order rate equation when high concentrations of tetralones, (10:1 mole ratio), are used.

$$r = k_{obs} \, [\text{Bromine}] \quad\quad\quad (5)$$

where $r = k_{obs} = K_{eq}k_1 \, [\text{Tetralone}]$

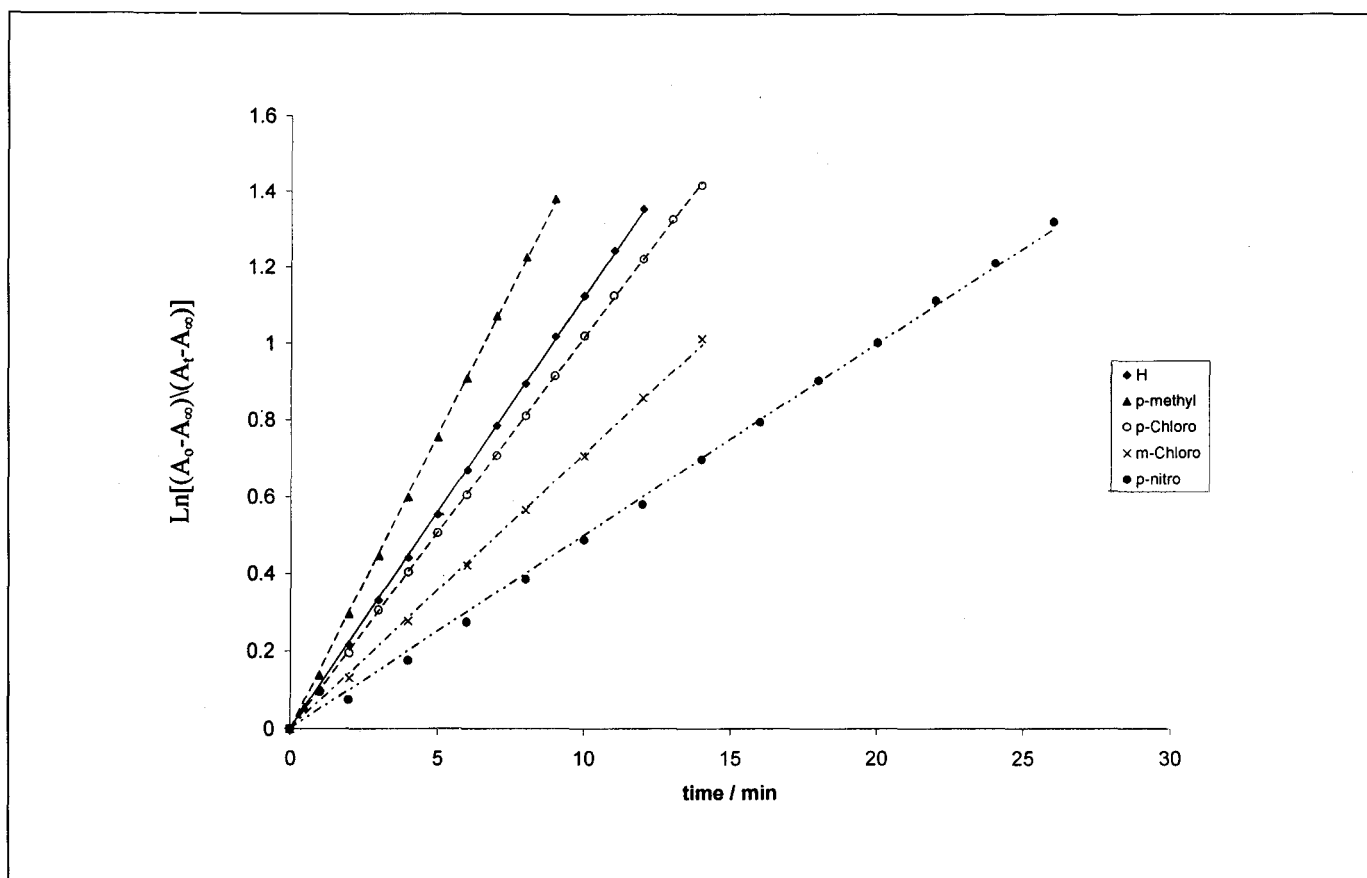The above two equations are quite consistent with the experimental results.

Fig. 1: Pseudo first order plot for the reaction of 2-benzal-1-tetralone and its derivatives I (1-5) with bromine in chloroform at
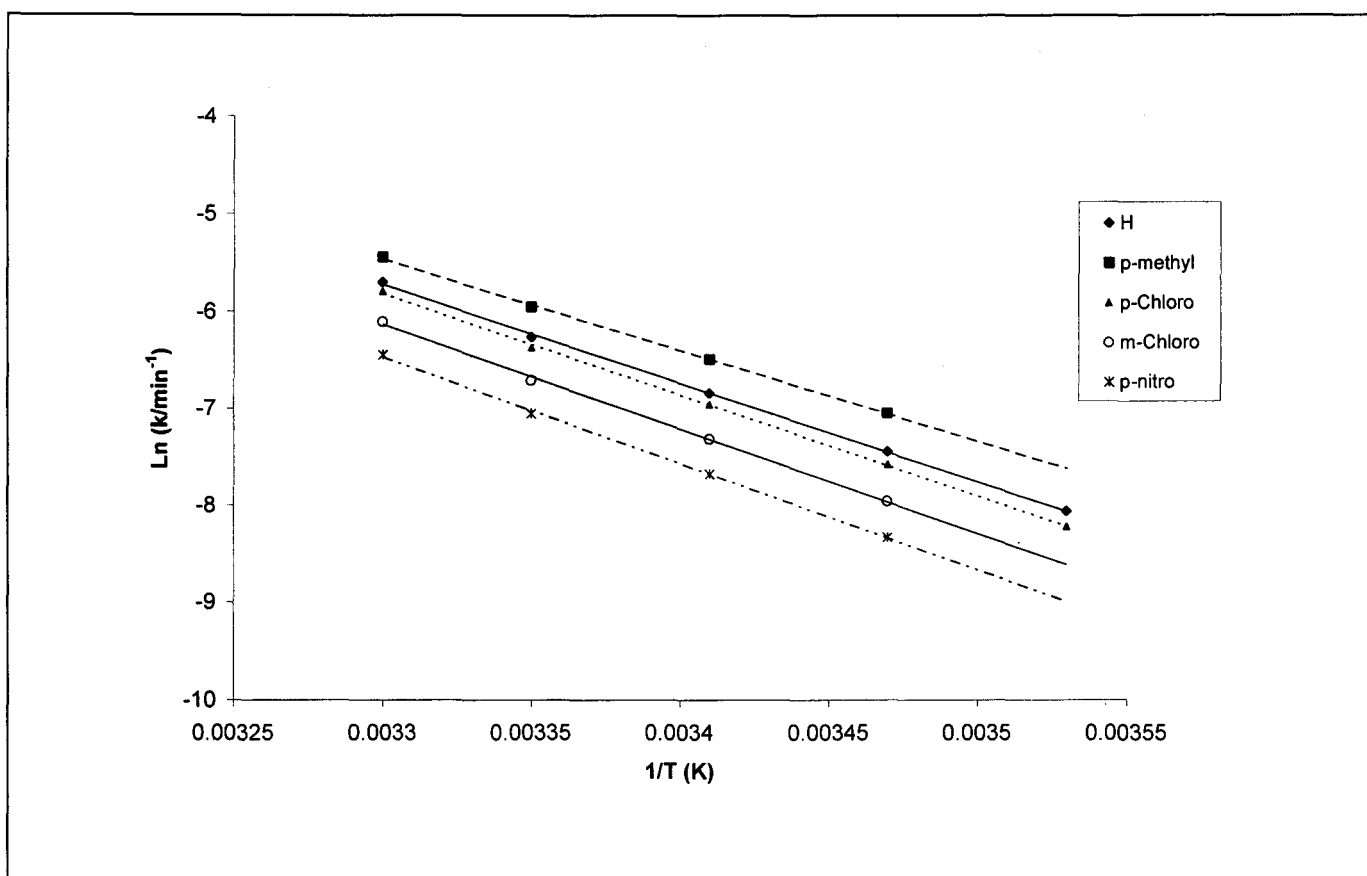

Fig. 2: Arrhenius plot for the reaction of 2-benzal-1-tetralone and its derivatives I (1-5) with bromine in chloroform.

Table 1 : Rate constants for reactions of I (1-5) with bromine at different temperatures.

Temp/°C	$10^4 k_{obs}/s^{-1} \pm 10^4 \sigma^* / s^{-1}$				
	1	2	3	4	5
	H	p-CH₃	p-Cl	M-Cl	P-NO₂
10	3.17 ± 0.00	----	2.71 ± 0.03	----	----
15	5.87 ± 0.01	8.68 ± 0.08	5.13 ± 0.01	3.50 ± 0.06	2.42 ± 0.00
20	10.67 ± 0.01	15.11 ± 0.03	9.48 ± 0.01	6.66 ± 0.06	4.64 ± 0.01
25	19.02 ± 0.04	25.93 ± 0.04	17.05 ± 0.04	12.21 ± 0.05	8.66 — 0.03
30	33.37 ± 0.03	43.00 ± 0.13	30.36 ± 0.04	22.30 ± 0.05	15.83 ± 0.02

* σ Is the standard error, see text.

Table 2 : Arrhenius parameters and entropies of activation for the reaction of I (1-5) with bromine.

Compounds	E_a / kJ.mol^{-1}	10^{-12} A – factor / s^{-1}	$\Delta S^{\#}$ 298 / J.mol^{-1}·K^{-1}
1. H	83.85	0.941	23.95
2. p-ch₃	77.25	0.095	43.58
3. p-Cl	86.09	3.280	17.32
4. m-Cl	89.06	5.770	10.13
5.p-NO₂	90.78	7.460	7.28

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