Sci. J. Fac. Sci. Monoufia Univ. Vol. VII (1993). 123 - 129

STUDIES ON BENZYLATION OF METHOXYPHENOL ISOMERS

Abd El-Aleem Hassan Abd El-Aleem

Faculty of Science, Menoufia University, Egypt

ABSTRACT

The benzylation reaction was studied by reaction of o-, m- and P-methoxyphenol with benzyl alcohol at 373 K and 393 K in the presence of polyphosphoric acid as catalyst. Kinetic studies of the reaction were achieved using gas-liquid chromatograph analyzer. The order of reaction, activation energy and suggested mechanism were considered.

EXPERIMENTAL

All experimental analyses were carried out using gas-liquid chromatography analyzer LXM-8 MD-3 (Model Russian), which has 3-copper tubes columns with length 300 cm, internal pore diameter 3 mm and full up by first (stelet-545 with liquid phase), second (stelet-545, 20% CKTØT-50X) and third (stelet-545, 20% apozon L).

Condition of analysis :

Column temperature is 220°C, detector (Katarometra) 250°C, dazatora 250°C, tok mosta 120 MA. inlet pressure 2 atom. and carrier gas, hydrogen 99.5% with speed 40 ml/min.

General method of benzylation:

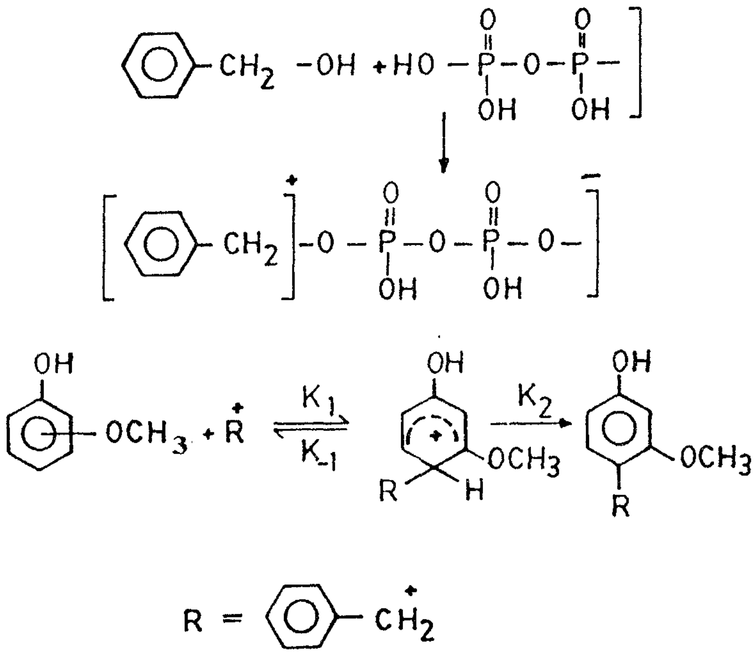
The reaction was carried out in a three-necked flask fitted with stirrer, condensers and a hole for introducing the reactants and withdrowing the samples. The flask was placed in a thermostatic oil

bath. The quantity of o-, m-, or p- methoxyphenol (2.16 g; 0.01 mol) was introduced followed by polyphosphoric acid(1.8 g; 0.01 mol). The reaction temperature was elevated to the desired level, then benzyl alohol (2.06 g; 0.01 mol) was added. The reaction temperature was maintained at the desired level. Samples were withdrown at different intervals. After cooling the samples, 0.1 ml of each sample was added to cold redestilled water (1 ml), with shaking for 5 minutes, then extracted with diethyl ether (1 ml). The extract was dried over anhydrous calcium chloride, then analyzed chromatographically according to the method described by Bakherev[1].

RESULTS AND DISCUSSION

In earlier studies [2-6], the alkylation of isomers of dimethoxybenzene with p- substituted benzyl alcohol was investigated using polyphosphoric acid and some other catalysts. In the present work, the reaction of o-, m- or p-methoxyphenol with benzyl alcohol, in the presence of polyphosphoric acid as a catalyst at two different temperatures (373 and 393 K) in molecular ratio (1:1), was investigated.

It is suggested that the reaction proceeds via intermediate formation of carbonium ion R^+. including the catalyst, followed by electrophilic attack on the methoxyphenol moiety, to obtained the benzylmethoxyphenol and separation of the catalyst.



The relations between the concentration of the products (mol/liter)and time (minutes) are shown in (Fig. 1) for reactions carried out at 373 K and (Fig. 2) for reaction carried out at 393 K. The derived kinetic curves are shown in (Fig. 3) and (Fig. 4), respectively.

The calculated rate constants and activation energies are tabulated in (table 1).

From (Figs. 3,4), it is clear that the benzylation is a second order reaction. The rate constant K can be calculated from the second order equation [7].

$$k = \frac{1}{t} \frac{C_x}{C_o (C_o - C_x)}$$

where C_x is the concentration after time t and C_o the initial concentration.

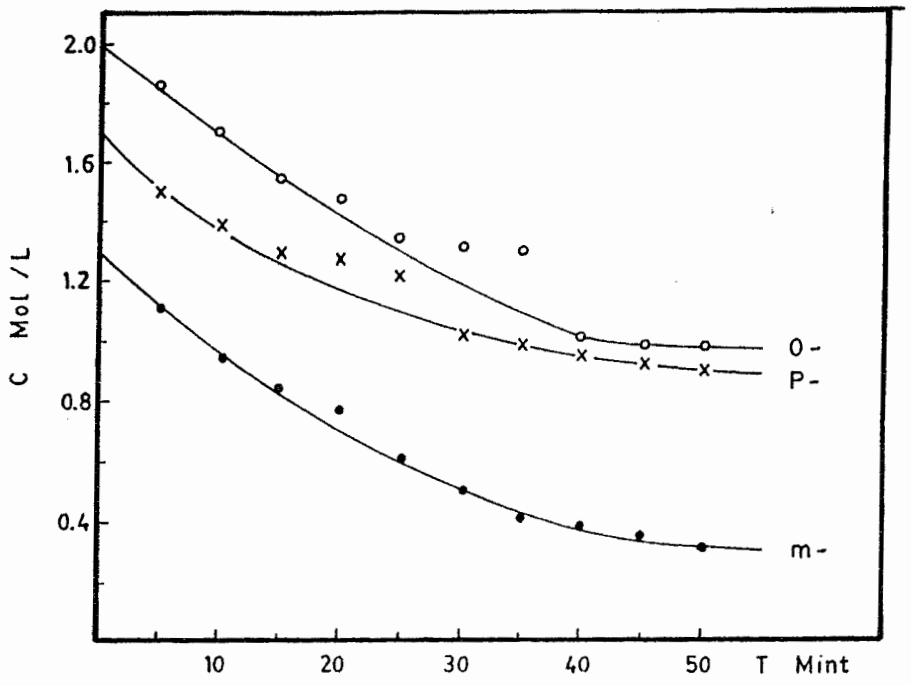

2.0
1.6
1.2
0.8
0.4
C Mol / L
10
20
30
40
50
T Mint
O-
P-
m-

Fig. 1.

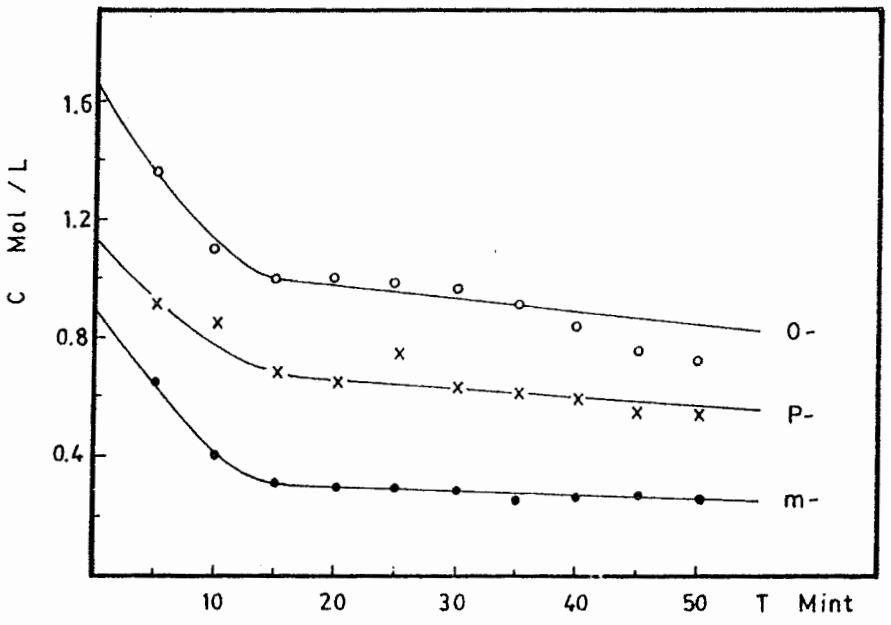

1.6
1.2
0.8
0.4
C Mol / L
10
20
30
40
50
T Mint
O-
P-
m-

Fig. 2.

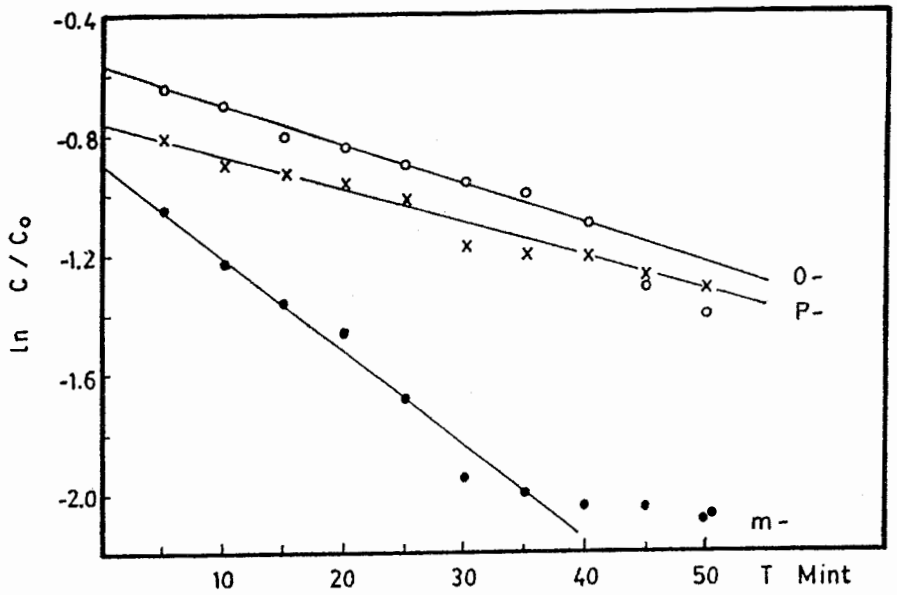

-0.4
-0.8
-1.2
-1.6
-2.0
Ln C / Co
O-
P-
m-
10
20
30
40
50
T Mint

Fig. 3.

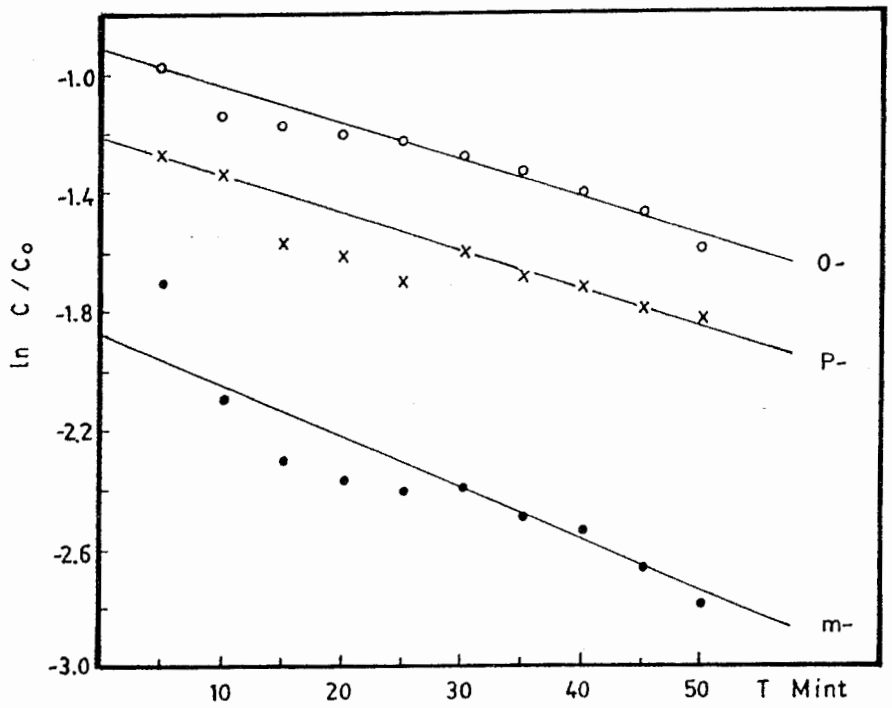

-1.0
-1.4
-1.8
-2.2
-2.6
-3.0
Ln C / Co
O-
P-
m-
10
20
30
40
50
T Mint

Fig. 4.

Table (1) :

	Rate Constant		Activation Energies
	373 K	393 K	k Cal/mol
m-Methoxyphenol	0.052	0.138	$9.698.10^3$
p-Methoxyphenol	0.029	0.062	$7.548.10^3$
o-Methoxyphenol	0.023	0.037	$4.723.10^3$

The present results show that the rate constant depends on temperature and the presence of catalyst. The activation energy was calculated from Arrhenius equation(8). The activation energy decrease in the order m- > p- > o- methoxyphenol. The variation in activation energy of substrate depend on distribution of charge density and also on stric consideration.

REFERENCES

1. Bakherev D.A. and Schyshnova A.F. "Advanced Study in Gas Liquid Chromatography" Meer Moscow (USSR) 125 (1975).
2. Brown H.C. and Neyns A.H.,J. Am. Chem. Soc., 84, 1233 (1962).
3. Inoveckia L.A., (Modern Theory in Organic Chemistry), Meer Moscow (USSR) 152 (1978).
4. Kohe H.J., U.S. Pat., 26, 2, 171, 420 (1955).
5. Huston R.C., Swartout H.A. and Wardwell G.K., J. Chem. Soc., 52, 93 (1930).
6. Huston R.C. and Lewis W.C., J. Am. Chem. Soc., 54, 1506 (1932).
7. Emanwal N.M. and Knoree D.G. "Course in Kinetics Chemistry). Meer Moscow (USSR) 75 (1969).
8. Denecov E.G. "Halogen Kinetics of Chemical Reactions", Meer Moscow (USSR) 17 (1978).

الملخص العربى

دراسات على بنزولة أيزميرات ميثوكس فينول

عبد العليم حسن عبد العليم
قسم الكيمياء – كلية العلوم – جامعة المنوفية

تمت دراسة تفاعلات البنزوله – بتفاعل أرثو – ، ميتا – ، بارا – ميثوكس فينول مع كحول البنزيل عند درجة حرارة ٣٧٣ ، ٣٩٣ درجة كلفينية مطلقة وذلك فى وجود حمض البولى فوسفوريك كعامل مساعد . وقد تمت هذه الدراسة بإستخدام جهاز الكروموتجراف السائل . وقد تم تعيين نظام التفاعل وطاقة التفاعل النشطة ، وميكانيكية التفاعل .