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KINETICS OF THE ACETYLATION OF SOME CONDENSED AND ISOLATED-RING HYDROCARBONS BY FRIEDEL-CRAFTS REACTION

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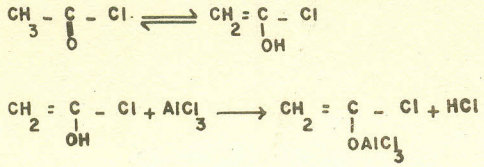
The rates and orders of reactions on the acetylation of biphenyl and *p*-terphenyl by acetyl chloride and anhydrous aluminium chloride according to Friedel-Crafts reactions in the highly polar solvent nitobenzene (34.83D at 25°) as well as the weakly polar solvent 1,2-dichloroethane (1OD) by the so-called complex I and II are studied together with the acetylation of naphthalene and anthracene in the latter solvent 1,2-dichloroethane. The rates and orders of reaction of the transformation of complex I to complex II in 1,2-dichloroethane as solvents are also studied and compared to the published results obtained for the same reaction in nitrobenzene as solvents.

All acetylation reaction in the polar solvent nitrobenzene are of a global orders one with respect to the acetylating complex and independent of the concentration of the aromatic hydrocarbon, while the global order is two in the weakly polar solvents 1,2-dichlorethane with partial first order respect to the aromatic hydrocarbon as well as the acetylating complex. The energies of activation and other thermodynamic parameters are calculated.

INTRODUCTION

It is generally accepted that the first stage in a Friedel-Crafts acetylation reaction is the interaction of the acid halide and aluminium halide to give an addition compound, of the oxonium form, which is considered to be the potential acetylating agent[1].

Illari[2] found that, in the case of acetylating aromatic hydrocarbons by easily enolised acid halides, two moles of HCl gas are evolved, and not one mole, per mole of hydrocarbon acetylated. He obtained the acetylating complex as a coloured viscous mass by working at 27°. The following is the probable reaction in the case of using acetyl chloride.



It follows, therefore, that acetylation of the aromatic hydrocarbon with the acetyl chloride-aluminium chloride adduct under conditions allowing its transformation to complex II (e.g. high temperatures and slow addition of the hydrocarbon) gives up to 2 moles of HCl gas which agrees with the findings of Illari[2], as well as the acetylation of naphthalene[3,4] and anthracene[5] by both complexes I and II in nitrobenzene.

A polar solvent such as nitrobenzene, dissolves, solvates and/or combines not only with $AlCl_3$, but also with $CH_3COCl.AlCl_3$ adduct and usually also with $AlCl_3$ complex with the resulting ketone[6,7]. The substituting agent can, therefore, be a larger complex incorporating nitrobenzene[8,9]. Such a bulky complex may be difficult to be substituted in the aromatic ring, e.g., in the α - position of naphthalene, thus the ratio of the β-acetyl naphthalene is higher when acetylation is carried out in the polar solvent nitrobenzene[10]. Baddeley[11] reported that 1,2-dichloroethane is the best solvent aluminium chloride-acetyl chloride complex. Bassiloios, Makar and Salem[12] tried to find a relation between the dipole moment of the solvent used and its effect on the α/β isomers ratio in the case of using naphthalene as the acetylated hydrocarbon. They proved that 1,2-dichloroethane (1.27 D) is a very suitable solvent since it dissolves the adduct rapidly as well as naphthalene.

The only studies on Friedel-Crafts acetylation reactions using 1,2-dichloroethane as solvent and aluminium chloride as catalyst reported in literature are those carried out by Corriu[13]. He reported a global order two.

In this work, the kinetic studies of the acetylation of the condensed ring aromatic hydrocarbons naphthalene and anthracene by complex I and II in 1,2-dichloroethane as solvent as well as the acetylation of the isolated aromatic hydrocarbons biphenyl and *p*-terphenyl by complex I and

II in nitrobenzene and in 1,2-dichloroethane are given.

EXPERIMENTAL AND RESULTS

The procedure and the apparatus used are the same as in previous publication[3,4,5]. The temperature used was not more than 14° to keep any change in the decomposition of the acetylating complex[4,14] at its minimum:

The suitability of the apparatus and accuracy of the runs checked by comparing the values obtained by:

1. total amount of alkali hydroxide consumed.
2. chloride ions in the titration vessel.
3. ketone yield.

Change of Complex I to Complex II in 1,2-Dichloroethane. Complex I is formed by the addition of acetyl chloride to $AlCl_3$ dissolved in 1,2-dichloroethane at lowest temperature possible (to avoid uncontrolled decomposition of the complex I). By raising the temperature to 6° and under pressure slightly lower than atmospheric (p=73.7 cm Hg) complex I was allowed to transfer to complex II with liberation of HCl in a measurable rate[4]. The reaction is of second order with an activation energy 25.08 K cal $mole^{-1}$. The specific velocities at different temperatures, the activation energy and other thermodynamic parameters are given in Table 1 together with the data of the same reaction in nitrobenzene as solvent for comparison.

Acetylation of Naphthalene and Anthracene by Complex I and II in 1,2-Dichloroethane. The global order of acetylation of naphthalene and anthracene by complex I and II in 1,2-dichloroethane are "two" with partial order "one" with respect to the aromatic hydrocarbon the acetylating complex. The specific velocities for the acetylation of naphthalene (0.1 to 0.3 $mole^{-1}$) and anthracene (less than 0.05 $mole^{-1}$) at different temperatures, the activation energies as well as other thermodynamic parameters are given in Table 2.

Isomer Distribution in the Acetylation of Naphthalene. Naphthalene can be acetylated either in α- or β- positions. The distribution ratio of the two isomers is influenced by the solvent used as well as by the temperature.

The isomer ratio was determined by the picrate method[11] whenever the product is liquid (mainly α- isomer) or/and the melting point procedure whenever the

Table 1. Effect of temperature on the specific velocities of the change of complex I into complex II in 1,2-dichloroethane and nitrobenzene, the activation energies and other thermodynamic paramters.

T°K	279	281	283	285	287	E K cal	ΔH*	ΔG* $mole^{-1}$	ΔS* eμ.
$C_6H_5NO_2^{(4)}$ k X 10^5	2.02	2.15	2.37	2.49	2.78	6.2	5.64	22.45	–59.4
$CH_2Cl–CH_2Cl$ k X 10^2	1.15	1.58	2.22	3.10	4.10	25.08	24.32	18.62	20.86

Table 2. Specific velocity constants at different temperatures, activation energies and other thermodynamic parameters for the acetylation of naphthalene and anthracene by complex I and II in 1,2-dichloroethane as solvent.

Complex	k X 10^2 $mole^{-1}$ L sec^{-1}					∡	YH*	ΔG*	ΔS*
T°K	279	281	283	285	287	Kcal	E	$mole^{-1}$	e.u.
Naphthalene									
I	1.12	1.41	1.77	2.24	2.85	18.30	17.74	18.74	–3.54
II	–	0.56	0.67	0.77	0.98	15.65	15.09	19.29	-14.84
Anthracene									
I	3.96	5.22	6.18	8.06	8.92	12.15	11.59	18.04	–22.80
II	1.40	1.94	2.66	3.68	4.88	25.63	25.07	18.52	–23.16

product is solid (mainly β-isomer).

The temperature effect on isomer distribution in the acetylation of naphthalene by complex I and II in 1,2-dichloroethane are given in Table 3.

Table 3. Temperatures effect on isomer distribution in the acetylation of naphthalene by complex I and II in 1,2-dichloroethane.

T°K	280	281	283	285	287
Complex I					
α%	98.2	98.0	97.8	97.6	97.4
β%	1.8	2.0	2.2	2.4	2.6
Complex II					
α%	99.0	98.5	98.1	98.0	98.0
β%	1.0	1.5	1.9	2.0	2.0

Acetylation of naphthalene and anthracene by Friedel Crafts reaction in nitrobenzene was previously studied kinetically [3,4,10]. The reaction are of global first order, being first order with respect to the acetylating complex and are independent of the concentration of the aromatic hydrocarbon. It was thought that extending the same work to poly nuclear isolated-ring aromatic hydrocarbons may be of interest. The aromatic hydrocarbons chosen are biphenyl and *p*-terphenyl. For the sake of comparison the same procedures and ranges of temperatures in previous work are used.

The Ketone Obtained. It is necessary, before the kinetic study, to make sure of the substitution taking place in these two hydrocarbons under the conditions of reaction used in the kinetic study.

Direct substitution in biphenyl with the usual electrophilic reagents given ortho and para mono-substituted products, one phenyl acting as an ortho-para group, for the substitution in the other[15]. One phenyl group behaves as an electron releasing group and the other as electron acceptor[16,17]. Acetylation of biphenyl by Friedel-Crafts reaction also gives the para mono acetyl derivative when almost equimolecular quantities of the reagents are used[18-20]. Substitution of a second acetyl group takes place in the para position of the second ring of the biphenyl molecule but this reaction requires rather strenous conditions, prolonged reaction with excess of aluminium chloride[21]. Silver and Lawy obtained the p-p' diacetyl biphenyl by using acetyl chloride two and half times that of the biphenyl and a six fold quantity of aluminium chloride[19,20].

Under the conditions used in this work (equimolecular concentration of reactants not exceeding 0.1 mole l^{-1}) substitution of a second acetyl group is so difficult as to be of no practical value. The ortho mono-acetyl ketone of biphenyl is also considered to be of minor effect in this work, due to difference of reactivities of the para and ortho positions[22].

Substitution in *p*-terphenyl should, therefore, be expected to occur predominantly in the para position with a minor substitution in the ortho position. The lower steric hinderance for the substitution in the ortho position [2,24] of the *p*-terphenyl due to the fact that the two terminal benzene rings are not coplanar with the central one is of minor effect due to interning resonance stabilization. We should, therefore, expect a *p*-substituted mono-acetyl ketone in the case of acetylation of *p*-terphenyl under mild conditions as that used in this work (equimolecular proportions of the reactants in dilute solution cir. 0.1 mole l^{-1} and temperature not higher than 14°).

If now remains to determine the number of acetyl groups per molecule of ketone obtained under the conditions of reaction used in this work. Melting point, molecular weight determination, spectrophotometric analysis and NMR spectra[23] showed that the product obtained under the conditions of the kinetic runs and in the same solvents is the mono-acetyl ketone.

The Kinetic Study of the Reaction. The rates of acetylation of biphenyl and *p*-terphenyl by (Friedel-Crafts) reaction using acetyl chloride-$AlCl_3$ complex I and II as the acetylating agents in nitrobenzene as solvent showed that the two reactions are of global first order, with partial orders one with respect to the aromatic hydrocarbon. The specific rates of the two reactions at different temperatures ranging from 6 to 14°, the activation energies and other thermodynamic properties are given in Table 4 obtained for the same reactions with naphthalane and anthracene under the same conditions[3, 4, 5] i.e., the reactions are of global second order and partial order one with respect to each of the reactants.

The specific rates, the activation energiers as well as other thermodynamic paramters are given in Table 4.

Acetylation of Biphenyl and p-*Terphenyl by Complex I and II in 1,2-Dichloroethane.* Acetylation of biphenyl and p-terphenyl by complex I and II in 1,2-dichloroethane under the same conditions used throughout this work gave the same orders of reaction as those in the case of naphthalene and anthracene i.e., a global second order reaction with partial orders one with respect to the acetylating complex and to the aromatic hydrocarbon but the specific rates, the activation energies and other thermodynamic parameters

Table 4. Specific rates at different temperatures, the activation energies and other thermodynamic parameters for the acetylation of biphenyl and p-terphenyl by complex I and II in nitrobenzene as solvent.

Complex	k x 10^4 sec^{-1}					E	ΔH*	ΔG*	ΔS*
T°K	279	281	283	285	287	Kcal	$mole^{-1}$		e.u
Biphenyl									
I	1.58	2.13	2.85	3.31	5.25	23.46	22.49	21.06	5.06
II	1.54	2.11	2.68	3.34	4.09	18.45	17.89	21.09	−11.30
p-terphenyl									
I	6.30	7.05	7.97	8.95	10.1	9.15	8.59	20.71	−42.02
II	4.55	6.37	6.17	7.27	8.54	12.77	11.12	15.46	−15.34

Table 5. Specific rates at different temperatures, the activation energies and other thermodynamic paramters for the acetylation of biphenyl and *p*-terphenyl by complex I and II in 1,2-dichloroethane as solvent.

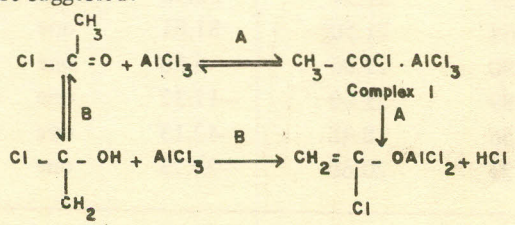
Complex	k X 10^3 $mole^{-1}$ l sec^{-1}					E	ΔH*	ΔG*	ΔS*
T°K	279	281	283	285	287	Kcal	$mole^{-1}$		e.u.
Biphenyl									
I	20.3	22.9	25.0	27.8	30.8	8.21	7.65	18.55	−38.51
II	4.7	5.55	6.20	7.19	8.45	11.47	10.91	19.33	−29.76
p-terphenyl									
I	20.5	25.8	32.3	40.6	49.4	18.07	17.51	18.41	− 3.17
II	7.9	11.25	15.65	22.40	29.35	27.36	26.80	18.81	28.23

are different. They are given in Table 5.

DISCUSSIONS

Change of Complex I to Complex II. It was found that acetyl chloride-aluminium chloride adduct of the oxonium form (Complex I) can be transformed to another complex with the liberation of one mole of HCl per mole of complex transformed[4] complex II, probably of the enol form, was found to acetylate the aromatic hydrocarbon with the liberation of another mole of HCl per mole of hydrocarbon acetylated which agrees with the findings of Illari[2].

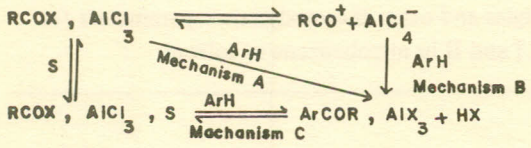
The transformation of complex I to complex II was found to be of the first order in nitrobenzen[4] and of second order in 1,2-dichloroethane. Two different mechanism are suggested:



Mechanism A in which complex I is a fast reaction and then is transformed to complex II with the liberation of HCl in a slow rate-determining step. This mechanism satisfies the first order rate while mechanism B in which the enolic form of the acid chloride combines with $AlCl_3$ with the liberation of HCl in a slow step satisfies a second order rate.

Mechanism is probably favoured when nitrobenzene is used as solvent which due to its high polarity (μ = 4.1), solvates the acetyl chloride-aluninum chloride complexes a bulky adduct is formed while mechanism B is favoured when 1,2-dichloroethane (μ = 1.27) is the solvent. The specific rates at different temperatures, the activation energies and the other thermodynamic paramters for the reaction in nitrobenzene and in 1,2-dichloroethane as solvent given in Table 6 support two different mechanism.

Mechanism of Acetylation of the Aromatic Hydrocarbon. Ketones of aromatic hydrocarbons can be formed by Friedel-Crafts synthesis following one of the three mechanisms A, B or C[23].



It is possible that the unsolvated acetylating complex is of high reactivity and medium steric requirements, that the acetylium ion is high reactivity and low steric requirements while the solvated acyl complex is of low reactivity and of large steric requirements.

The mechanisms A, B and C are not merely alternatives but may proceed simultanously, their relative importance being a function of the reactivities of reactants and the solvating power of the solvent "S".

In nitrobenzene as solvent, the global orders of the acetylation reactions of naphthalene[3, 4], anthracene[5], biphenyl[24] and *p*-terphenyl[25] are all first order with partial order "one" with respect to the acetylating complexes, whether complex I or II, while the concentrations of the aromatic hydrocarbons have no effect on the rate of reaction (Table 7).

Using 1,2-dichloroethane as solvent for the same reaction, they become of second order[24-27].

The solvent used also found to influence the order of reaction for the transformation of complex I to complex II and the acetylation of the aromatic hydrocarbon by complex II in the same way.

The solvent, therefore, influences the order of reaction and, consequently, the mechanism followed. Anous and coworkers[3] gave an ionic mechanism for the acetylation of naphthalene by complex I in the polar nitrobenzene as solvent which is nearly similar to mechanism B, with the exception that acyl carbonium ion is solvated. This results in a bulky solvated less reactive acetylating ion which is obtained[10].

The mechanism (S_N1), therefore, probably the same in the acetylation of the four hydrocarbons studied in the same polar solvent nitrobenzene since the reactions have the same global and partial order "2", the weakly polar solvent 1,2-dichloroethane, the acetylation reactions of the same aromatic hydrocarbons by complex I and II are all of global second order with partial order one with respect to

Table 6. Effect of temperature on specific rates, activation energies and other thermodynamic parameters for the transformation of complex I to complex II.

T°K	279	281	283	285	287	E Kcal	ΔH*	ΔG* mol^{-1}	ΔS* e.u.
k.10^5 ($C_6H_5NO_2$)	2.02	2.15	2.37	2.49	2.78	6.2	5.24	22.45	–59.4
k.10^2 (CH_2ClCH_2Cl)	1.15	1.58	2.22	3.10	4.10	25.08	24.52	18.62	20.86

Table 7. Specific velocities, activation energies, other thermodynamic parameters and order of reaction for the acetylation of aromatic hydrocarbon in nitrobenzene at 10°C.

Hydrocarbon	Complex	k.10^4 sec^{-1}	E Kcal	ΔH*	ΔG* mole^{-1}	ΔS* e.u.	Order
Naphthalene	I	0.99	13.70	13.14	21.65	-30.07	one
	II	0.45	47.50	46.94	22.10	87.84	one
Anthracene	I	1.63	12.80	12.24	21.37	-32.25	one
	II	1.20	45.20	44.64	21.50	81.61	one
Biphenyl	I	2.85	23.46	22.90	21.06	6.50	one
	II	2.68	18.45	17.89	21.09	–11.32	one
p-terphenyl	I	7.97	9.12	8.56	18.48	–42.13	one
	II	6.17	12.77	12.21	20.60	–29.73	one

Table 8. Specific velocities, activation energies, other thermodynamic parameters and order of reaction for acetylation of some aromatic hydrocarbon in 1,2-dichloroethane at 10°

Hydrocarbon	Complex	$k.10^2$ mole^{-1} 1 sec^{-1}	E Kcal	ΔH^* mole^{-1}	ΔG^*	ΔS^* e.u.	order
Naphthalene	I	1.77	18.30	17.74	18.74	- 3.54	two
	II	0.67	15.65	15.09	19.29	14.83	two
Anthracene	I	6.18	12.15	11.59	18.04	22.80	two
	II	2.66	25.63	25.07	18.52	23.16	two
Biphenyl	I	2.50	8.21	7.65	18.55	–38.52	two
	II	0.62	11.47	10.91	19.33	–29.76	two
p-terphenyl	I	3.23	18.07	17.51	18.41	– 3.17	two
	II	1.57	27.36	26.80	18.81	28.23	two

the acetylating complex as well as the acetylated aromatic hydrocarbons. The acetylating agent in the case of complex I in this weakly polar solvent is probably the unsolvated acetyl chloride-$AlCl_3$ adduct which should be more active than the solvated adduct since the electron demand is not affected[27]. The slow step in this mechanism is probably the formation of the ketone complex which fits the order of the reaction and is similar to mechanism "A" given above (S_N2).

Comparative Study of the Acetylation of Condensed and Isolated-ring Aromatic Hydrocarbons. Considering the values of specific rates of acetylation of the studied four aromatic hydrocarbons by complex I and II in nitrobenzene as solvent (Table 7), it is clear that complex II is less active as acetylating agent than complex I in each case. This is also shown by considering the values of activation energies "E" (with the exception of biphenyl). The same trend is also found when 1,2-dichloroethane is the solvent, but the rates of acetylation in this solvent are much higher than in nitrobenzene which agrees with the idea that the solvation of the acetylium ion, when an ionic mechanism is suggested when complex I is the acetylating agent, or the solvation of acetyl chloride–$AlCl_3$ adduct, result in decreasing the reactivity of the acetylating agent.

The reactivity of aromatic hydrocarbons acetylating by the same complex, in nitrobenzene as solvent (Table 5) increases in the following order: Naphthalene < anthracene < biphenyl < *p*-terphenyl. Examination of the activation energies of these reactions show that they are 13.7 and 12.8 K cal. mole^{-1} when acetylating naphthalene and anthracene by complex I and 47.50 and 45.20 K cal. mole^{-1} when acetylating them by complex II respectively.

When acetylating biphenyl and *p*-terphenyl by complex I the activation energies are 23.46 and 9.12 while they are 18.42 and 12.77 when acetylating the same hydrocarbons by complex II respectively. This show that the decrease in the values of activation energies agree with the increase of the specific rates in the case of condensed ring hydrocarbons naphthalene and anthracene as well as in the case of the isolated ring hydrocarbons biphenyl and *p*-terphenyl.

In 1,2-dichloroethane as solvent the reaction is faster when acetylating the hydrocarbon using complex I than when complex II is the acetylating agent. This again agrees with the variation in the activation energies for the acetylation of the condensed-ring hydrocarbons (except in case of naphthalene) and isolated ring hydrocarbons.

While complex I is more reactive than complex II in all cases, yet the difference between the activation energies for the acetylation by complex I and II in case of condensed ring hydrocarbons naphthalene and anthracene in nitrobenzene as solvent (Table 7) are greater than those for the acetylation of isolated ring hydrocarbons biphenyl and *p*-terphenyl (except in case of biphenyl).

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