

Kinetics Decomposition of Some Substituted Benzenediazonium Salts in HCl Solution.

Khulood Al-saadie, Israa M. Al-Mousawi and Nadia Abdul karime
Department of Chemistry, College of Science University of Baghdad, Jadiriya, Baghdad, Iraq.

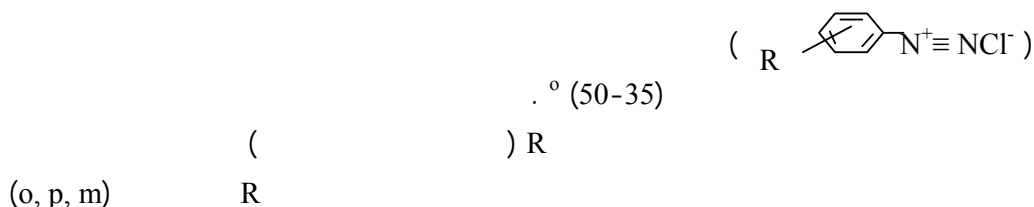
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Abstract

The decomposition rate, rate constant and decomposition activation energy of substituted benzenediazonium salts ($\text{R-C}_6\text{H}_4\text{N}_2^+ \equiv \text{NCl}^-$) were calculated by following the quantity of nitrogen gas produced as a function of time at several temperatures ranging from (35 to 50)°C. The effect of the R group type on the rate of decomposition, rate constant and activation energy, was studied. The effect of variation of R group position (o, p, m) has been studied as well.

Keywords : Diazonium salts, kinetics, Substituted effect, SN^1 .



Introduction

The Aromatic diazonium ions are stable in cold solution. The solid diazonium salts are very dangerous, explosive and rarely can be separated and some diazonium salts are cancerous⁽¹⁾. In an acidic aqueous solution, benzenediazonium ion (pH_2N_2^+) will decompose⁽²⁾ to form nitrogen and phenol:
 $\text{C}_6\text{H}_5\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{N}_{2(\text{g})} + \text{H}^+ \dots \dots (1)$

The rate of reaction (1),- $d(\text{C}_6\text{H}_5\text{N}_2^+)/dt$, can be written in terms of the concentration of the reacting species as:

$$-d(\text{C}_6\text{H}_5\text{N}_2^+)/dt = k^1(\text{C}_6\text{H}_5\text{N}_2^+)^n (\text{H}_2\text{O})^m \dots \dots (2)$$

As written above, the reaction would be of n th order with respect to $\text{C}_6\text{H}_5\text{N}_2^+$ and of m th order with respect to water, and would have an overall order of (n+m).

The reaction is not acid-catalyzed⁽³⁾, although very high acid concentrations (say 12N HCl) seem to slightly increase the rate⁽²⁾. Thus the effect of changes in the H^+ concentration due to reaction (1) can be completely neglected. Since the present experiment will be performed in a dilute aqueous solution, the concentration of water (H_2O) will be very nearly constant throughout the reaction. Thus the factor $(H_2O)^m$ can be absorbed into the rate constant and Eq. (2) can be rewritten as:

$$-dc/dt = kC^n \dots\dots(3)$$

Where C represents the instantaneous concentration ($C_6H_5N_2^+$). Eq.(3) can readily be integrated to give:

$$C = C_0 e^{-kt} \quad \text{for } n=1 \quad \dots\dots(4)$$

If the value of a rate constant is measured at several different temperatures, it is almost always found that the temperature dependence can be represented by:

$$k = A e^{-E^*/RT} \dots\dots(5)$$

Where the factor A is independent of temperature, the Arrhenius activation energy E^* can be easily determined by plotting $\log k$ versus $1/T$. This should give a straight line with slope $(-E^*/2.303 R)$.

Rate of reaction can be established by means of other than simple chemical determination of concentration, after various time intervals, of residual starting materials. Thus in the reaction (1), the volume of gaseous nitrogen evolved may be measured directly with a burette or a gas syringes, i.e at constant pressure.

Experimental Procedure

The progress of the reaction is studied by measuring the quantity of gas produced as a function of time. At any given time, the volume of nitrogen evolved is directly proportional to the number of moles of benzenediazonium chloride (or substituted benzenediazonium chloride ($R-\text{C}_6\text{H}_4-\text{N}_2^+\text{Cl}$), that have decomposed. The rate of the reaction is therefore proportional to the rate of nitrogen evolution. The apparatus used in this experiment is shown in Fig.1.

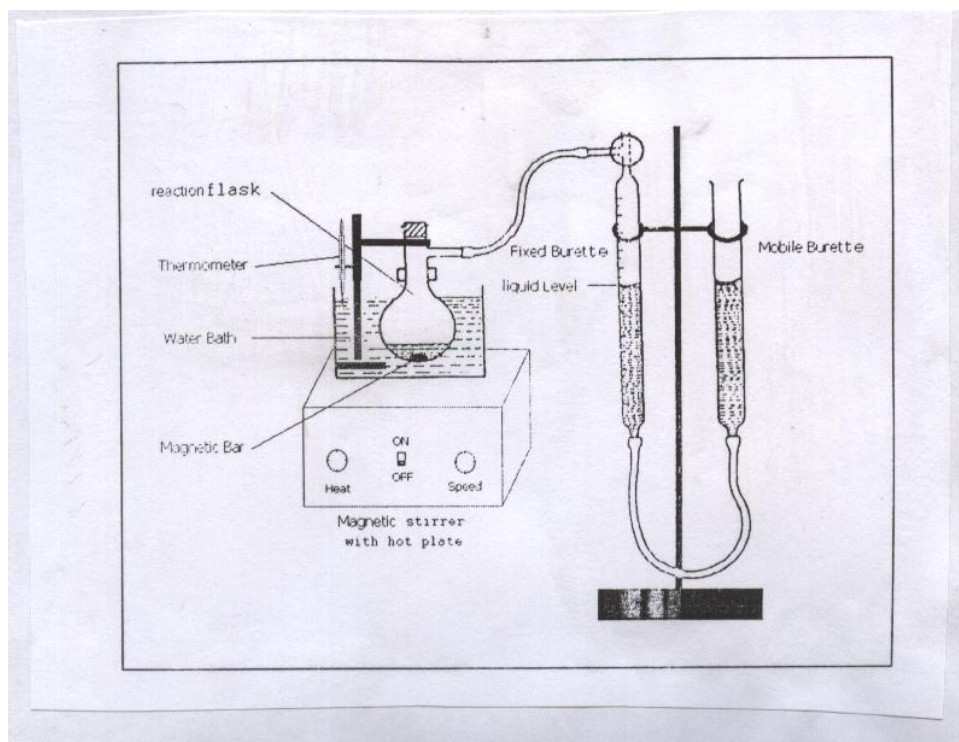


Fig.1: Apparatus for studying the rate of evolution of gas.

The reacting solution is attached to the gas burette. The incoming gas depresses the liquid level. To measure the volume of gas at any time, the leveling mobile burette is raised or lowered until the liquid is at the same level in both burette. At that moment, the burette reading and the time are both recorded. The pressure of nitrogen in the burette is atmospheric pressure minus the vapor pressure of water in the burette. Since the vapor pressure of water is constant during the run, the nitrogen pressure is also constant and the burette reading is directly proportional to the amount of nitrogen produced and therefore to the quantity of benzenediazonium decomposed.

Requirements

Small round bottom flask with side arm connected to Hempel gas burette Fig. 1, magnetic stirrer hot plate, magnetic stirring bar, thermometer, {aniline, p-chloro aniline, p-nitro aniline, p-amino benzoic acid, o-amino phenol, m- amino phenol, p-amino phenol, m-Toluidine, o- Toluidine, p-Toluidine} all chemicals were of purum grade, obtained from Fluka with high purity ranging (98-99.9)%. The procedure includes the following steps:

- 1- 1.6 g of aniline or substituted aniline dissolved in few volume of methanol and 5 ml conc. HCl in ice bath.
- 2- Cold solution of 1.8 g NaNO_2 in 18 mL H_2O at 5°C , was added to the

first step slon. drop by drop, then the volume completed to 250 mL by distilled water.

- 3- 50 mL from each solon. prepared was used in each experiment for each temperature and the decomposition is carried out at different temperatures ($35\text{-}50$) $^\circ\text{C}$ for each diazonium salt derivative.

Measurements and Results

The volume of N_2 as a function of time was taken periodic at four temperature with stirring the flask in the water bath. The readings were continually until less than 0.5 ml of gas generated per 2 min. interval.

Without detaching the flask from the burette, the reaction mixture was heated in a beaker of boiling water for about 1 min. in order to decompose the unreacted salt, then the flask cooling down to 35°C before reading the final volume. This step was repeated at $40, 45, 50^\circ\text{C}$. The reaction is first order with respected to diazonium salt, and the kinetic equation expressed as ⁽⁴⁾:

$$\text{Log}(V_\infty/V_\infty - V_t) = \frac{kt}{2.303} \dots\dots\dots (6)$$

Where V_∞ = final gas volume at ∞ time
 V_t = volume at time t.

The slope of the graph is $k/2.303$, where k is the specific rate constant (k/min^{-1}). Figs.(2-3) show a liner relations between $\text{log}(V_\infty/V_\infty - V_t)$ at four temperatures, and the data are shown in Table 1.

Table 1 experimental values for all compounds at different temperatures (35-50) °C

Compound	308.15 K			313.15 K			318.15 K			323.15 K		
	Time	$V_{\infty}-V_T$	LOG ($V/V_{\infty}-V_T$)	Time	$V_{\infty}-V_T$	LOG ($V/V_{\infty}-V_T$)	Time	$V_{\infty}-V_T$	LOG ($V/V_{\infty}-V_T$)	Time	$V_{\infty}-V_T$	LOG ($V/V_{\infty}-V_T$)
Aniline	1	72	0.0617	1	54.6	0.1819	2	48	0.2378	1	41	0.3063
	7	66	0.0995	9	44	0.2756	6	31	0.4277	4	31	0.4277
	12	60	0.1409	14	37	0.3509	11	21	0.5969	8	19	0.6403
	15	54	0.1867	18	28	0.4719	14	14	0.7729	11	11	0.8777
	21	43	0.2856	23	20	0.618	17	7	1.0739	13	5	1.2201
p-chloro aniline	1	26	0.2382	1	56.4	0.0271	1	65.4	0.042	1	18	0.4576
	3	22	0.3108	3	49.8	0.0813	3	53.9	0.1261	3	10	0.8129
	7	18.7	0.3814	7	38.8	0.1896	7	36.6	0.2941	8	5	1.1139
	12	17	0.4228	13	26.7	0.3522	13	20.5	0.5464	15	2	1.5118
p-nitro aniline	1	64	0.1232	1	49	0.2392	1	40	0.3274	1	30	0.4997
	5	53	0.2051	3	40	0.3273	3	21	0.6072	4	21	0.6546
	8	45	0.2762	5	32	0.424	7	12	0.8502	8	8	1.0737
	10	40	0.3274	8	23	0.5677	10	4	1.3274	12	2	1.6758
	13	35	0.3854	13	17	0.6989						
p-amino benzoic acid	1	67	0.1424	1	59.3	0.1714	1	51	0.2369	1	46	0.2817
	3	61	0.1736	3	48	0.2632	4	39	0.3534	2	39	0.3534
	5	51	0.2048	5	42.8	0.313	7	26	0.5295	4	25	0.5465
	8	46	0.2516	8	37	0.3763	9	20	0.6435	6	17.2	0.7089
	14	42	0.3452				15	10.5	0.9233	11	11	0.9031
p-amino phenol	1.5	87.1	0.00931	1	54	0.2169	1	48.7	0.3391	1	41	0.3366
	3	85.3	0.01863	5	40	0.3473	5	32.5	0.4083	7	17	0.7189
	8	79.4	0.04967	10	32	0.4442	13	20	0.5467	11	12	0.8702
	12	75	0.07452	18	26	0.5344	26	17	0.7716	18	7	1.1043
				26	23	0.5877						
o-amino phenol	1	38	0.2264	1	33	0.2808	1	28	0.4279	1	28	0.4666
	3	34	0.27	3	21	0.4771	3	18	0.6198	5	13	0.7998
	8	29	0.3438	7	15	0.6232	7	8	0.9719	10	2	1.6128
	17	23.8	0.4296	12	10	0.7993	12	5	1.1761			
	36	23	0.4445	19	2	1.4983						
m-amino phenol	1	63	0.0504	1	61	0.1641	1	38	0.4025	1	24.1	0.6003
	5	43	0.3452	6	33	0.4309	3	21	0.6601	2	13.1	0.865
	10	25	0.7137	11	11	0.908	5	13	0.8683	3	6.1	1.1969
	14	11	1.0085	15	6	1.1712	7	7	1.1372			
	16	4	1.1559									
p-Toluidine	1	25	0.2552	5	25	0.4082	1	36	0.3934	1	39.6	0.2921
	3	16	0.449	10	17	0.5757	2	21	0.457	4	27.6	0.4489
	7	13	0.5392	15	11	0.7647	6	12	0.7114	8	9.6	0.9075
	13	10	0.6532	20	7.7	0.9196	12	6.2	1.093	15	0.6	2.1117
	20	6.3	0.8538	25	5.8	1.0427						
o-Toluidine	1	76.4	0.02031	1	78.7	0.0335	1	80.9	0.0511	1	77.8	0.07763
	5	63.4	0.1016	3	62.5	0.1007	3	63.9	0.1532	3	54.4	0.2329
	8	55.1	0.1625	7	49.5	0.2351	6	44.9	0.3064	5	38.1	0.3881
	13	44.1	0.2641	10	39.3	0.3358	10	28.1	0.5103	9	18.6	0.6987
	18	34.5	0.3656	15	26.6	0.5039	13	19.9	0.6621	11	13.1	0.8539
m-Toluidine	1	61	0.1123	5	53	0.0108	1	39.8	0.2866	1	57.7	0.2023
	5	52	0.1816	9	40	0.186	3	24	0.5063	4	14.3	0.8094
	12	43.8	0.2562	16	28	0.4926	7	13	0.7725	12	1	2.4283
	19	34	0.3661	26	17	0.9306	13	5	1.1875			
	29	26.8	0.4695	38	3	1.4562						
	42	22	0.5552									
	54	16	0.6935									

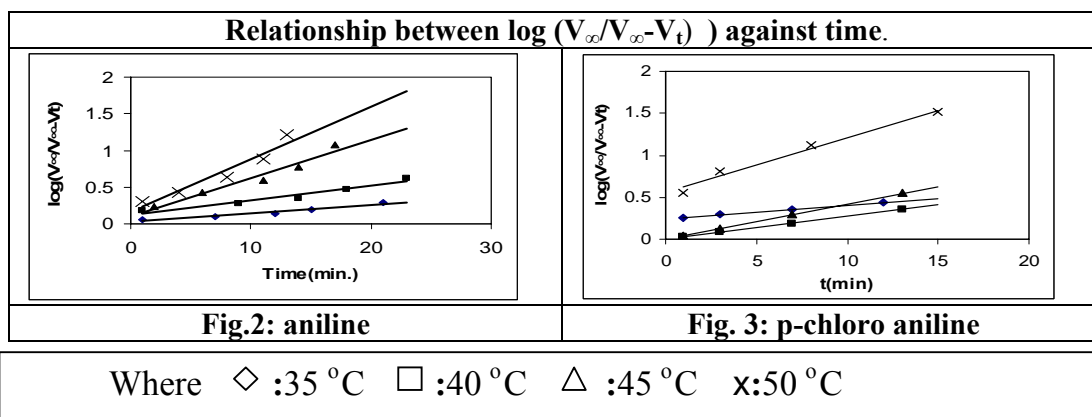


Table 2 gives the rate constant values calculated from Fig.(2-3), at four temperatures. Generally k (rate constant) increases with temperature, and a linear relations were obtained when plotted the

logarithm of k against $1/T$, (T/k), and the activation energy, Arrhenius constant were obtained from the slope and intercept respectively (eq. 5).

Table 2 Values of rate constants for all compounds.

No.	Compound	$k \text{ (min)}^{-1}$ at different temperatures (K)			
		T=308.15	T=313.15	T=318.15	T=323.15
1	Aniline	0.02556	0.04514	0.1198	0.1649
2	p-chloro aniline	0.03685	0.06241	0.0967	0.1502
3	p-nitro aniline	0.05112	0.08959	0.2379	0.2485
4	p-amino benzoic acid	0.03593	0.0654	0.1154	0.1449
5	p-amino phenol	0.0143	0.03247	0.03984	0.1025
6	o-amino phenol	0.01359	0.14439	0.1571	0.2966
7	m-amino phenol	0.1697	0.1822	0.2777	0.6870
8	p-Toluidine	0.06448	0.07369	0.1465	0.3079
9	o-Toluidine	0.04675	0.07738	0.1172	0.1787
10	m-Toluidine	0.02441	0.10087	0.1681	0.4661

Figs. (4-5) show the Arrhenius relations for the decomposition of the ten diazonium salts prepared in this study. Table 3 gives the E_a (kJmol^{-1}) and $\log(A/\text{min}^{-1})$ for the ten reactions.

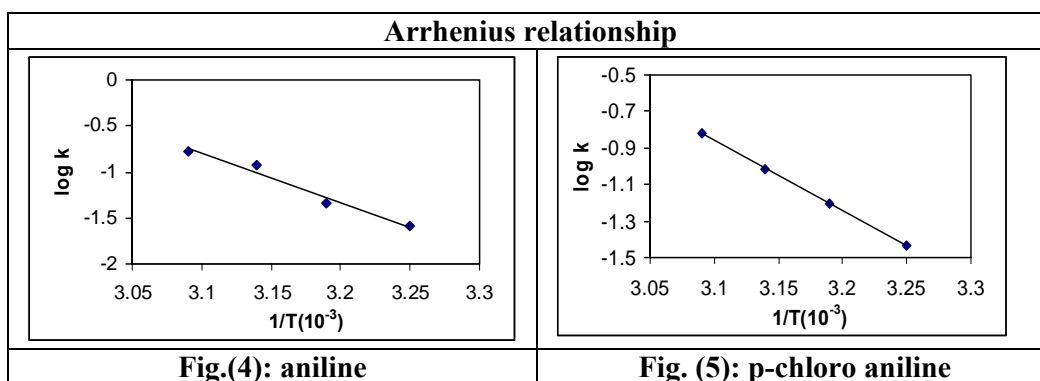


Table 3 Values of activation energy and Arrhenius constants for all compounds.

No.	Compound	E_a (kJmol ⁻¹)	Log A
1	Aniline	102.893	15.86
2	p-chloro aniline	73.019	10.96
3	p-nitro aniline	89.932	13.99
4	p-amino benzoic acid	74.842	19.96
5	p-amino phenol	95.929	14.44
6	o-amino phenol	159.844	25.50
7	m-amino phenol	71.086	11.20
8	p-Toluidine	83.177	12.84
9	o-Toluidine	69.634	10.49
10	m-Toluidine	147.519	23.48

Discussion

A linear relationship was found to exist between the experimental values of log

A and the corresponding values of E_a as in Fig. 6. which could be expressed as ⁽⁵⁾:

$$\text{Log A} = I + m E_a \quad \dots\dots\dots (7)$$

Where I and m are a constant.

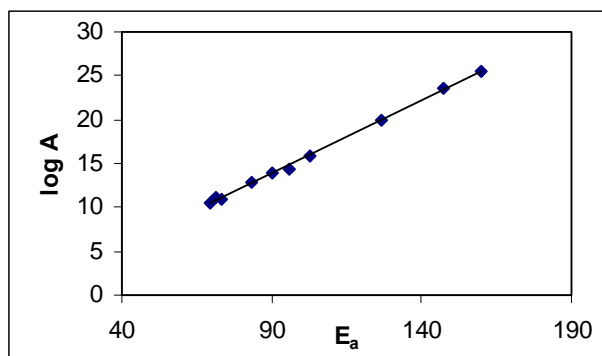


Fig.6 relationship between log A and E_a (kJmol⁻¹) for all salts.

Where m and I are respectively the slope and the intercept of the plots in Fig.6. Such a relationship is termed a "Compensation effect" which is frequently found to describe the kinetics of catalytic reactions ⁽⁶⁻⁸⁾. Equation (7) shows that simultaneous increases in E and log A for a particular system tend to compensate from the standpoint of reaction rate. In order for a reaction to take place, free energy of activation $\Delta^\ddagger G$ must be added. When a reaction has progressed to the point corresponding to the top of the curve, the term transition state is applied to the positions of the nuclei and electrons. The transition state possesses a definite geometry and charge distribution but has no finite existence.

The system at this point is called an activated complex. In the transition – state theory the starting materials and the activated complex are taken to be in equilibrium. According to the theory, all activated complexes go on to product at the same rate, so that the rate constant of the reaction depends only on the position of the equilibrium between the starting materials and the activated complex. Like ΔG , $\Delta^\ddagger G$ is made up of enthalpy and entropy components.

$$\Delta^\ddagger G = \Delta^\ddagger H - T\Delta^\ddagger S \quad \dots\dots\dots (8)$$

$\Delta^\ddagger H$ the enthalpy of activation, is the difference in bond energies, including strain, resonance, and solvation energies, between the starting compounds and the transition state. In many reactions bonds have been

broken or partially broken by the time the transition state is reached; the energy necessary for this is $\Delta^{\#}H$. It is true that additional energy will be supplied by the formation of new bonds, but if this occurs after the transition state, it can affect only ΔH and not $\Delta^{\#}H$. Entropy of activation $\Delta^{\#}S$, which is the difference in entropy between the starting compounds and the transition state. Table (4) shows the $\Delta^{\#}G$, $\Delta^{\#}H$ and $\Delta^{\#}S$ for the decomposition of the ten diazonium salts prepared in this study. $\Delta^{\#}S$ calculated from Arrhenius constant (eq. 5), using the following equation⁽¹⁷⁾:

$$\log A = \log \frac{kT}{h} + \frac{\Delta^{\#}S}{2.303 R} \dots\dots\dots (9)$$

Where; k , is Boltzman constant; T is the temperature in K; h plank constant and R is gas constant.

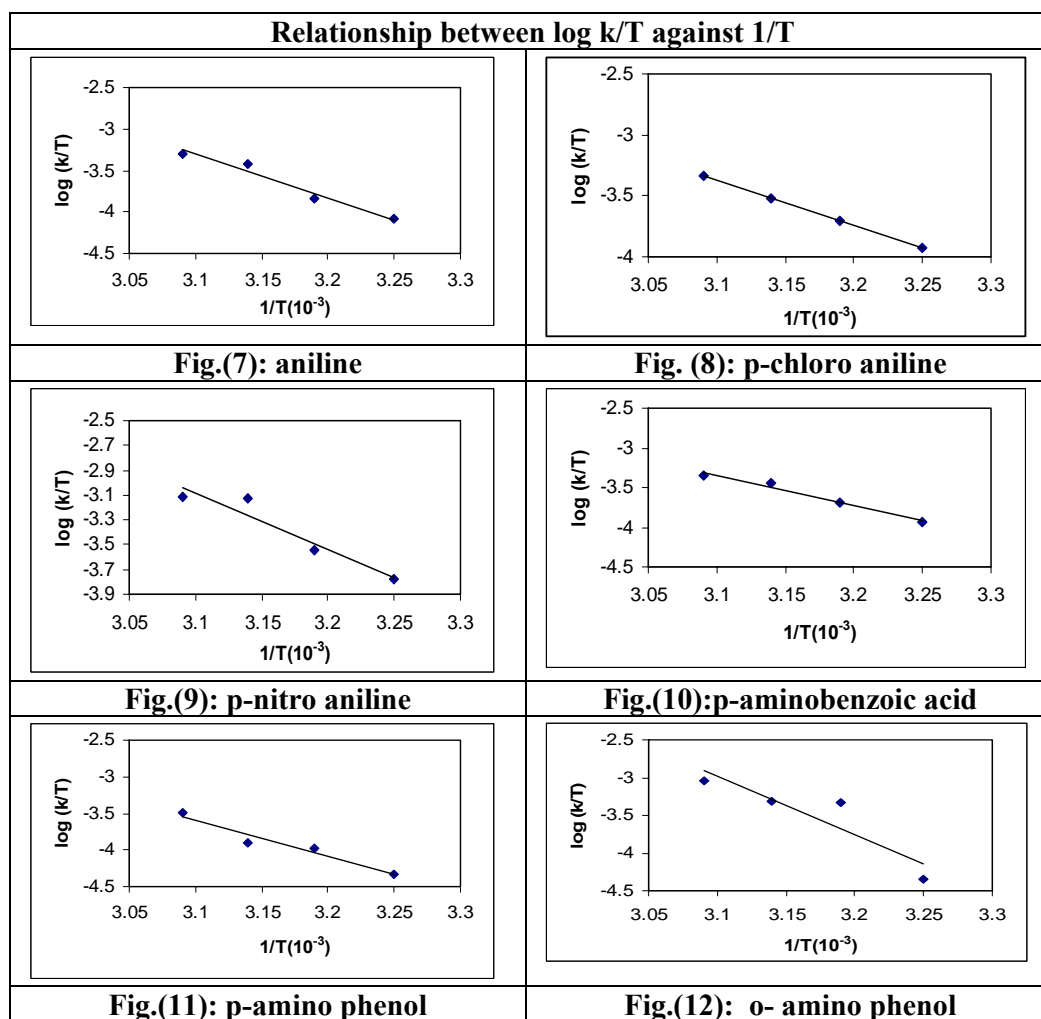
Arrhenius eq. can be written:

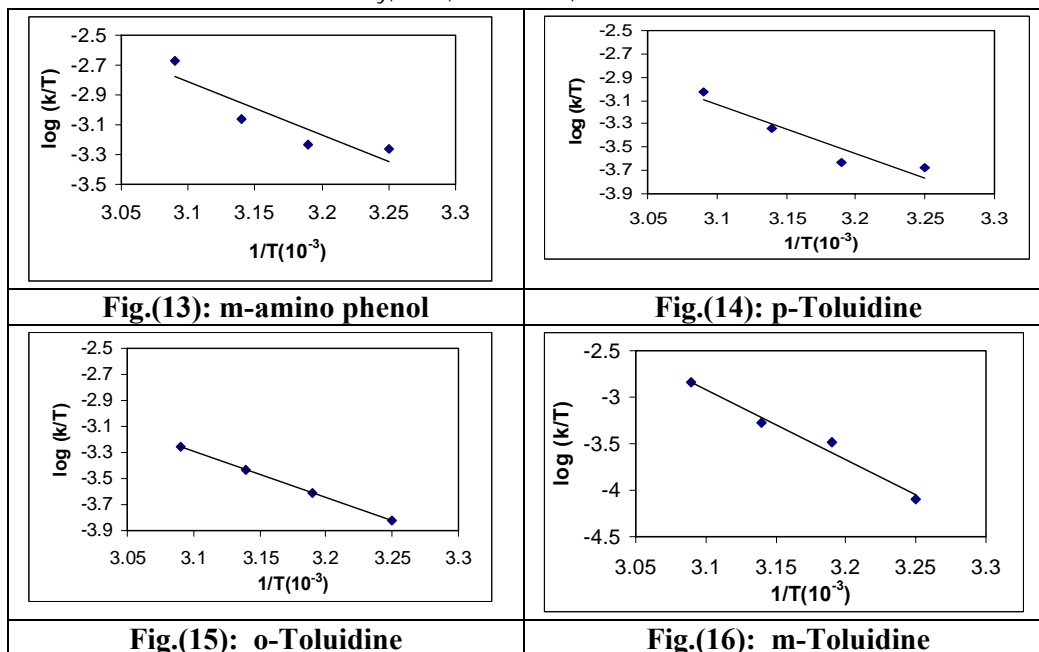
$$k = \frac{kT}{n} e^{-\Delta^{\#}H / RT} e^{\Delta^{\#}S / R} \dots\dots\dots (10)$$

$$\log \frac{k}{T} = \log \frac{k}{h} + \frac{\Delta^{\#}S}{2.303n} - \frac{\Delta^{\#}H}{2.303n} \cdot \frac{1}{T} \dots\dots\dots (11)$$

$$\Delta^{\#}H = 2.303 m_2 R \dots\dots\dots (12)$$

Where m_2 is the slope of a liner relation between $\log k/T$ and $1/T$ as shown in Figs. (7-16).





$\Delta^{\#}G$ calculated from eq. 8. Table (4) shows that o-amino phenol have a highest $\Delta^{\#}S$ while o-Toluidine have the lowest value. The existence of $-OH$ group in the ortho position (o-amino phenol) cause to increase $\Delta^{\#}H$ for aniline from $100.415 \text{ kJmol}^{-1}$ to $147.027 \text{ kJmol}^{-1}$.

In general the electron rich benzene ring stabilizes the $-N^{\oplus} \equiv N$ group as shown in Table (3), where $-CH_3$ group in m-Toluidine increase the E_a from $102.893 \text{ kJmol}^{-1}$ for

aniline to $147.519 \text{ kJmol}^{-1}$ for m-Toluidine. Also $-OH$ group increase E_a for o-amino phenol to $159.844 \text{ kJmol}^{-1}$. While the groups with drawing like $-Cl$ group decrease the stability of the ring and the activation energy for p-chloro aniline decreases to $73.019 \text{ kJmol}^{-1}$. The difference in the position, (o, p or m) causes a large differences in the stability of the ring and then in the activation energy of the decomposition of the salt as shown in Table (4).

Table 4 Thermodynamic values for the compounds.

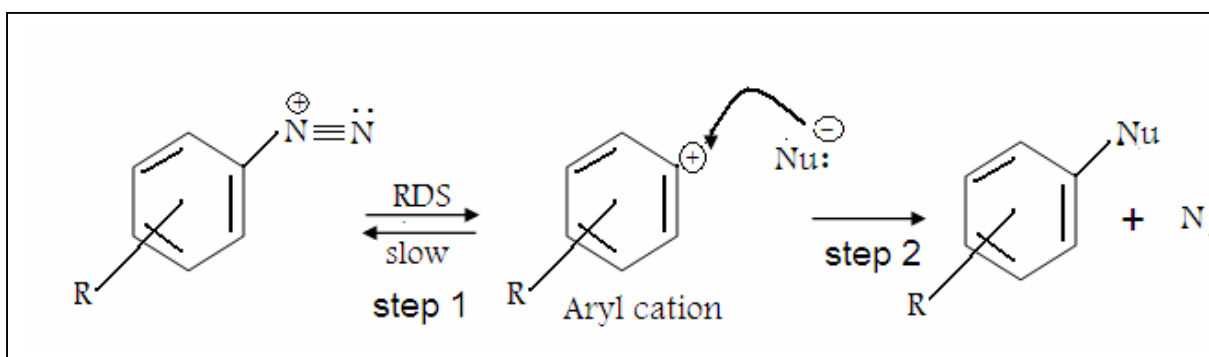
No.	Compounds	$\Delta^{\#}H$ kJmol^{-1}	$\Delta^{\#}S$ $\text{JK}^{-1}\text{mol}^{-1}$	$\Delta^{\#}G_{308}$ kJmol^{-1}	$\Delta^{\#}G_{313}$ kJmol^{-1}	$\Delta^{\#}G_{318}$ kJmol^{-1}	$\Delta^{\#}G_{323}$ kJmol^{-1}
1	Aniline	100.415	50.429	84.875	84.623	84.371	84.119
2	p-chloro aniline	70.544	-43.393	83.915	84.132	84.349	84.566
3	p-nitro aniline	87.447	14.490	82.982	82.909	82.837	82.764
4	p-amino benzoic acid	72.3685	-37.271	83.856	84.042	84.229	84.415
5	p-amino phenol	93.444	23.183	86.299	86.184	86.068	85.952
6	o-amino phenol	147.027	200.963	85.100	84.096	83.091	82.086
7	m-amino phenol	68.606	-38.778	80.556	80.750	80.944	81.137
8	p-Toluidine	80.665	-7.467	82.966	83.003	83.041	83.078
9	o-Toluidine	67.208	-52.250	83.309	83.570	83.832	84.093
10	m-Toluidine	145.042	196.215	84.578	83.597	82.616	81.635

Fig.17 The variation of the $\Delta^\ddagger S$ and $^\ddagger E_a$ for the decomposition of the ten salts prepared in this study.

$\Delta^\ddagger S$ (JK ⁻¹ mol ⁻¹)	6	6	$\Delta^\ddagger E_a$ (kJmol ⁻¹)
	10	10	
	1	1	
	5	5	
	3	3	
	8	8	
	4	4	
	7	2	
	2	7	
	9	9	

Fig.17: variation of the $\Delta^\ddagger S$ and $^\ddagger E_a$ for the ten salts prepared from compounds (1-10).

The most important mechanism for the decomposition of diazonium salt is (S_N^1) mechanism⁽⁹⁾. The nitrogen molecule lost from diazonium salt.

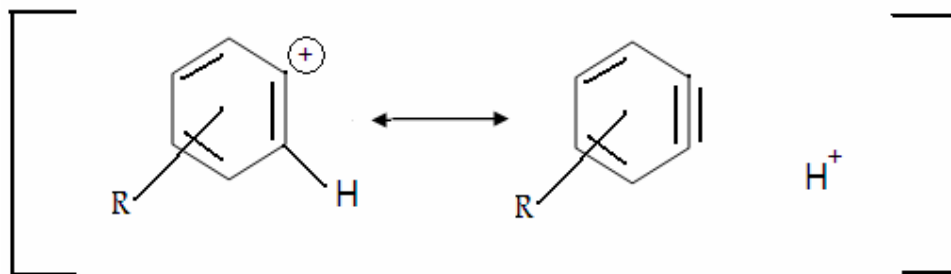


The most important evidence for this reaction mechanism comes from kinetic studies that indicate that the reaction is first order in diazonium salt, so the slow step of the reaction is the decomposition of the salt. Since the nucleophile is not involved in the RDS (Rate Determining Step), the reaction is actually an S_N^1 reaction for aromatic substitution. Among the evidence for the S_N^1 mechanism with aryl cations as intermediates⁽¹⁰⁾, is the following⁽¹¹⁾:

- 1- The reaction rate is first order in diazonium salt and independent of concentration of nucleophile.
- 2- When high concentrations of halide salts are added, the product is an aryl

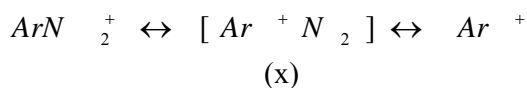
halide but the rate is independent of the concentration of the added salts.

- 3- The effects of ring substitutions on the rate are consistent with a unimolecular rate-determining cleavage⁽¹²⁾.
- 4- When reactions were run with substrate in the ortho position, isotope effects of about 1.22 were obtained⁽¹³⁾. It is difficult to account for such high secondary isotope effects in any other way except that an incipient phenyl cation is stabilized by hyper conjugation, which is reduced when hydrogen is replaced by deuterium.



5- That the first step is a reversible cleavage⁽¹⁴⁾ was demonstrated by the observation when $\text{Ar}^{15}\text{N}^+\equiv\text{N}$ was the reacting species recovered starting material contained not only $\text{Ar}^{15}\text{N}^+\equiv\text{N}$ but also $\text{ArN}^+\equiv^{15}\text{N}$. This could arise only if the nitrogen breaks away from the ring and then returns.

Additional evidence was obtained from $\text{phN}=\text{N}^{15}$ with unlabeled N_2 at various pressures. At 300 atm the recovered product had lost about 3% of the labeled nitrogen, indicating that phN_2^+ was exchanging with atmospheric N_2^{15} . There is kinetic and other evidence⁽¹⁶⁾ that step 1 is more complicated and involves two steps, both reversible:



(x) is probably some kind of a tight ion-molecule pair.

Conclusions

The reaction of the decomposition of diazonium salt is of first order and S_N^1 mechanism. The $-\text{CH}_3$ and $-\text{OH}$ groups lead to more stability of the salts with activation energy, $147.519 \text{ kJmol}^{-1}$, $159.844 \text{ kJmol}^{-1}$ respectively with compare for aniline with $E_a=102.893 \text{ kJmol}^{-1}$.

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