Kinetic Investigation of Oxidation of Aromatic Anils by Potassium Peroxymonosulfate in Aqueous Acidic Medium

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ABSTRACT: The kinetics of oxidation of aromatic anils to benzaldehyde and azobenzene by potassium peroxymonosulfate has been studied in aqueous acetic acid medium. The low dielectric constant of the medium facilitates the reactivity. It has been found that the variation in the ionic strength of the reaction has a negligible effect on the rate. Similarly, polymerization was not observed when acrylonitrile was added to the reaction mixture. This observation rules out the formation of any free radical in the reaction. The added Mn(II) increases the rate of the reaction, which indicates the involvement of two-electron transfer. Highly negative $\Delta S^{\#}$ values indicate a structured transition state. The deviation of the Hammett plot was noted, and a concave downward curve was obtained for the anils with substituents in the aniline moiety. The observed break in the log k_{obs} versus σ is attributed to the transition state whereas the concave upward curve was observed for the substituents in the benzaldehyde moiety and in the combination of aniline and benzaldehyde moieties, and a suitable mechanism was proposed. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 45: 542–550, 2013

INTRODUCTION

Peroxymonosulfate (PMS) is used as a powerful oxidant for a wide variety of industrial and consumer applications [1]. PMS often oxidizes faster than hydrogen peroxide and is slightly more powerful as an oxidant ($E_{\text{HSO}_{5}^{-}/\text{HSO}_{4}^{-}}^{0} = +1.82 \text{ V}; E_{\text{H}_{2}\text{O}_{2}/\text{H}_{2}\text{O}}^{0} = +1.76 \text{ V}$) [2]. When used in organic synthesis as an oxidant, PMS is found to be more efficient than hydrogen peroxide or persulfate [3]. Broad applications of potassium peroxymonosulfate (PPMS), an efficient oxidant, have been performed in organic synthesis recently due to its versatility, stability, operation simplicity, nontoxicity, and low costs [4]. PPMS is obtained as a mixture of KHSO₅–K₂SO₄–KHSO₄. The triple salt, 2KHSO₅–K₂SO₄–KHSO₄, is commercially known as Oxone, which is a monosubstituted derivative of H₂O₂. Thus, it is thermodynamically more powerful as an oxidant than H₂O₂ and kinetically more reactive. In acid medium, the triple salt gives the active "HSO₅–

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HSO₅⁻" a potentially important strong oxidant, which is first described in the oxidation reactions [5,6] and some of the later studies including the oxidations of aldehydes [7], [(NH₃)₅CoS₂O₃]⁺ [8], amino acids [9], sulfide ion [10], tris(2,2-bipyridyl)Ru(II) [11], Ti(III), Fe(II), and α -oxygen–substituted radicals [12], NO₂⁻ ion [13], parasubstituted anilines [14], aminobenzoic acids [15], "Co²⁺" ion in the presence of molybdate ion, [16], and that of $[Co(II)W_{12}O_{40}]^{6-}$ [17]. Schiff bases are nitrogen donor ligands (-CH=N-) that form complexes by donating an electron pair to a metal atom in the formation of coordination compounds. Schiff bases have found wide applications in the field of coordination chemistry [18], biological processes [19], several enzymes [20], microcalorimetry [21], cytotoxic [22], insulin mimetic agents [23], anticonvulsant [24], antiproliterative [25], antifungal activities [26], "transport of oxygen in mammalian," and other respiratory systems [27]. Aromatic anils, X-CH=N-Y have two phenyl rings X and Y, the ring X originates from the aromatic benzaldehyde moiety and Y from the aniline moiety. It is possible to evaluate the reaction constant (ρ) from the Hammett plot by varying the substituents in one of the rings X or Y, and keeping the same substituent in the other ring. It is therefore possible to get several reaction constants for different substituents in one of the two rings. The kinetics and mechanism of oxidation of some substituted anils, using several oxidants, have been reported [28-37]. A literature survey reveals that no report is available on the kinetics of oxidation of meta- and parasubstituted aromatic anils with PPMS; hence it is worthwhile to do research on the kinetics and mechanism of oxidation of anils by PPMS.

EXPERIMENTAL

Anils were prepared [38] by refluxing equimolar quantities of benzaldehyde and aniline in ethanol for about 2-3 h. The resulting solution was cooled and poured into cold water. The precipitated anil was filtered off, washed with ethanol, and dried. It was recrystallized from ethanol. The purity of the anils was checked by determining their melting points and FT-IR spectrum (mp 53°C [lit. 54°C]), microanalysis Found: C 86.10, H 6.02, N 7.68; calculated: C 86.18, H 6.07, N 7.73. All other chemicals used were of analytical grade (Merck, Mumbai, India). Acetic acid was purified by redistillation. All the reagents were prepared just before the reactions were carried out. The aqueous solution of PPMS (Sigma Aldrich, Bangalore, India) was prepared fresh and standardized iodometrically. All the reactions were carried out in a thermostat, and the temperature

was controlled to $\pm 0.1^{\circ}$ C. The reactions were performed under pseudo-first-order conditions by maintaining excess of anil over the oxidant. The mixture was homogeneous throughout the course of the reaction. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically at regular time intervals. The rate constants (k_{obs}) were obtained from log (titer) versus time plots. All the rate constants were averages of two or more determinations. Under kinetic conditions, stoichiometric amounts of the substrate and PPMS were mixed. After 24 h, the acetic acid was neutralized and the reaction mixture ethanol was extracted. The dark brown extract, when subjected to thin-layer chromatography, gave two distinct spots. On evaporation of ethanol, the products were found to be benzaldehyde, which was confirmed by the isolation of its 2,4-dinitrophenylhydrazone derivative and azobenzene identified by its melting point and a UVvis spectrum. The λ_{max} of azobenzene was confirmed by comparing with that of the authentic sample in aqueous acetic acid medium.

The oxidation reactions of meta- and parasubstituents of aromatic anils were studied at different temperatures (298, 303, 308, 313, and 318K) to evaluate various thermodynamic parameters. From the Eyrings equation [39], the thermodynamic parameters, enthalpy of activation, and entropy of activation are calculated from the following expression:

$$k_{\rm obs} = (k_{\rm b}T/h) \exp^{\Delta G^{\#}/RT}$$

where k_b is Boltzmann's constant, *T* is the temperature in kelvin, *h* is plank's constant, and *R* is the gas constant. $\Delta G^{\#}$ is the activation of Gibbs free energy, and the energy of activation (*E*_a) can be calculated from the following expressions, respectively:

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S$$
$$E_{a} = \Delta H^{\#} + RT$$

where $\Delta H^{\#}$ is the enthalpy of activation and $\Delta S^{\#}$ is the entropy of activation.

RESULTS AND DISCUSSION

The reaction followed first-order kinetics with respect to the concentration of anil and PPMS, respectively. Under the identical experimental conditions [Anil] \gg [PPMS], the pseudo–first-order linear plot of log (titer) versus time is linear upto 90%, depicted in Fig. 1. The order in [Anil] was first, as revealed by the slope of the plot of log k_{obs} against log [Anil]



Figure 1 Pseudo-first-order plot for PPMS oxidation of aromatic anil at 308 K.



Figure 2 Plot of log k_{obs} versus log [Anil] at 308 K.

(Fig. 2), with the correlation coefficient (r = 0.996). The kinetic order in acidity appears to be unity but increases in $[H^+]$; the rate of the reaction was decreased. The kinetic results are summarized in Table I. The ionic strength of the reaction varies by the addition of Na₂SO₄, and its influence on the reaction rate was studied and has been found that it has no significant effect on the reactivity. No polymerization with acrylonitrile was observed. Addition of Mn(II) increases the rate of the reaction, and the rate data are listed in Table II. Temperature dependence studies were conducted for all the substituted anils (substitution in X and Y ring separately) between 298 and 318 K. The rate constants for the reaction systems and activation parameters were evaluated from the Eyring plots as listed in Table III. When an attempt was made to fit in the rate data of meta- and parasubstituted anils (substitution in the aniline moiety and benzaldehyde moiety separately and substitution

Table I	Effect of Varying the Concentration of Anil,
PPMS, H	2SO4, and Solvent Composition on the Rate at
308 K	

[Anil] (×	[PPMS] (×	[H ⁺]	HOAc	$k_{\rm obs}$ (×
10^2 mol dm^{-3})	10^3 mol dm^{-3})	$(mol dm^{-3})$	(%)	10^4 s^{-1})
6.0	5.0	1.0	50	3.66
7.0	5.0	1.0	50	4.57
8.0	5.0	1.0	50	4.93
9.0	5.0	1.0	50	5.81
10.0	5.0	1.0	50	6.50
11.0	5.0	1.0	50	7.25
8.0	3.0	1.0	50	4.88
8.0	4.0	1.0	50	4.79
8.0	5.0	1.0	50	4.93
8.0	6.0	1.0	50	4.86
8.0	7.0	1.0	50	4.91
8.0	8.0	1.0	50	4.72
8.0	5.0	0.8	50	6.22
8.0	5.0	0.9	50	5.68
8.0	5.0	1.0	50	4.93
8.0	5.0	1.1	50	4.42
8.0	5.0	1.2	50	4.09
8.0	5.0	1.0	30	5.65
8.0	5.0	1.0	40	4.83
8.0	5.0	1.0	50	4.57
8.0	5.0	1.0	60	4.35
8.0	5.0	1.0	70	3.91

Table IIEffect of [Mn(II)], [Acrylonitrile], $[Na_2SO_4]$ onthe Reaction Rate at 308 K

[Mn(II)] (mol dm-3)	[Acrylonitrile] (mol dm ⁻³)	$[Na_2SO_4] (mol dm^{-3})$	$k_{\rm obs} (\times 10^4 {\rm s}^{-1})$
0	_	_	4.93
0.02	_	_	5.62
0.04	_	_	6.41
0.06	_	_	7.22
0.08	-	-	7.87
_	0	_	4.93
_	0.02	_	5.07
_	0.04	_	5.01
_	0.06	_	4.88
_	0.08	-	4.99
_	_	0	4.93
_	_	0.02	5.22
_	_	0.04	5.41
_	-	0.06	5.74
-	-	0.08	5.87

 $[Anil]=0.08\ mol\ dm^{-3};\ [PPMS]=0.005\ mol\ dm^{-3};\ [H_2SO_4]=1.0\ mol\ dm^{-3};\ HOAc\ -H_2O\ =\ 50\%\ (v/v);\ temperature\ =\ 308\ K.$

in both aniline and benzaldehyde moieties) into the Hammett equation, a concave downward curve was obtained for the anils with substituents in the aniline moiety, whereas the concave upward curve was observed for the substituents in the benzaldehyde

				$k_{\rm obs}$	$(\times 10^{-4} s)$	s ⁻¹)		∧ <i>H</i> #	-^?#	#5V	E _o (kJ		
Moiety	S. No.	Substituents	25°C	30°C	35°C	40°C	45°C	$(kJ mol^{-1})$	$(J K^{-1} mol^{-1})$	$(kJ mol^{-1})$	$mol^{-1} K^{-1}$	r	SD
Aniline	-	H	4.72	5.64	6.50	7.17	9.69	23.52	229.87	94.32	25.90	0.976	0.06
	7	m-CH ₃	3.23	3.56	4.48	5.02	8.59	33.47	200.39	95.19	35.85	0.935	0.15
	с	p -CH $_3$	4.40	4.38	4.64	4.92	5.84	8.09	282.58	95.12	10.47	0.849	0.06
	4	p-OC ₂ H ₅	3.46	3.87	3.83	6.08	7.67	29.46	213.29	95.15	31.84	0.917	0.15
	5	p -OCH $_3$	3.03	3.45	4.18	4.49	6.27	24.40	230.84	95.49	26.78	0.967	0.07
	9	p-Cl	4.40	5.93	7.13	7.85	20.40	49.87	142.80	93.85	52.25	0.902	0.28
	7	m-Cl	4.51	5.11	5.92	7.23	12.40	34.56	194.01	94.31	36.94	0.932	0.16
	8	$m-NO_2$	6.18	6.38	8.59	9.32	11.00	21.55	234.52	93.78	23.93	0.967	0.06
	6	$p-NO_2$	3.79	5.04	5.83	14.40	22.40	69.66	78.18	93.73	72.04	0.958	0.24
Benzaldehyde	-	Н	4.72	5.64	6.50	7.17	9.69	23.52	229.87	94.32	25.90	0.986	0.06
·	7	m-CH ₃	6.08	6.89	7.67	10.70	14.40	31.39	201.96	93.59	33.77	0.963	0.10
	с	p -CH $_3$	5.32	7.06	9.73	11.90	13.60	35.33	188.88	93.50	37.71	0.989	0.06
	4	p-OC ₂ H ₅	7.41	10.70	14.50	24.80	30.40	55.20	119.88	72.25	57.58	0.993	0.07
	5	p -OCH $_3$	13.80	19.50	21.70	24.40	32.00	27.53	206.99	91.28	29.91	0.974	0.07
	9	p-Cl	4.44	5.45	5.86	6.38	25.30	54.15	129.30	93.97	56.53	0.992	0.03
	7	m-Cl	4.51	5.51	6.77	8.29	12.60	36.10	188.41	94.13	38.48	0.980	0.08
	8	$m-NO_2$	6.02	6.23	8.64	9.22	11.40	23.68	227.63	93.79	26.06	0.967	0.05
	6	$p-NO_2$	5.23	7.93	11.50	22.50	37.40	75.76	54.37	92.50	78.14	0.992	0.11
In both aniline and benzaldehyde	1	Η	4.72	5.64	6.50	7.17	9.69	23.52	229.87	94.32	25.90	0.976	0.06
	7	m -CH $_3$	3.61	3.86	4.42	5.51	6.31	20.56	242.36	95.20	22.94	0.956	0.05
	3	p -CH $_3$	4.98	5.42	6.55	10.90	12.20	36.60	186.30	93.98	38.98	0.956	0.13
	4	p-OC ₂ H ₅	6.35	7.19	8.07	14.70	18.50	42.20	165.67	93.32	44.58	0.949	0.16
	5	p -OCH $_3$	10.90	14.80	17.80	22.00	24.60	29.45	202.56	91.83	31.83	0.988	0.05
	9	p-Cl	7.55	9.40	10.40	10.90	11.50	13.10	260.35	93.28	15.48	0.929	0.06
	7	m-Cl	4.59	5.63	7.35	8.37	11.00	31.21	204.29	94.13	33.59	0.995	0.04
	8	$m-NO_2$	6.13	7.85	8.25	9.14	10.50	16.83	249.72	93.74	19.21	0.967	0.05
	6	$p-NO_2$	3.58	5.11	6.99	8.59	13.90	48.34	148.87	94.19	50.72	0.992	0.07
$[Anil] = 0.1 \text{ mol } dm^{-3}; [PPMS] =$	0.005 mol	dm^{-3} ; $[H_2SO_4] =$	= 1.0 mol	dm ⁻³ ; HC	$Ac - H_2O$	= 50% (v/v).						

 Table III
 Temperature Effect and Thermodynamic Parameters of PPMS Oxidation of Anils

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Agatia	Dialaatria	k. (x
Acid (%)	Constant (D)	$10^4 \mathrm{S}^{-1}$
30	56.83	5.65
40	49.60	4.83
50	42.37	4.57
60	35.14	4.35
70	27.90	3.95

Table IVPseudo–First-Order-Rate Constants for theOxidation of Anils by PPMS in Different Acetic AcidCompositions

$$\label{eq:anil} \begin{split} [Anil] &= 0.1 \text{ mol } dm^{-3}; \\ [PPMS] &= 0.005 \text{ mol } dm^{-3}; \\ [H_2SO_4] &= 1.0 \text{ mol } dm^{-3}; \\ HOAc - H_2O &= 50\% \ (v/v). \end{split}$$

moiety and a concacve upward curve was observed for the substituents in the combination of aniline and benzaldehyde moieties.

Effect of the Dielectric Constant

The effect of solvent on the reaction rate was studied by varying the composition of acetic acid from 30%to 70% (Table IV). The oxidations were carried out by maintaining the concentration of anils and PPMS and temperature constant. The above observation clearly reveals that the rate decreases with an increase in the percentage of acetic acid, i.e., with decreasing dielectric constant (*D*) or low dielectric constant or polarity of the medium. This directs to the conclusion that there is a charge development in the intermediate state involving a more polar intermediate than reactants, suggesting a polar (ionic) mechanism. The low dielectric constant of the medium facilitates the reactivity.

Mechanism

The known fact is that the free radicals can be produced by the homolytic fission of peroxide bond. An acrylonitrile monomer is having capability to trap the free radicals with the formation of polymer. But, in the oxidation reaction it does not form any polymer (no formation of turbidity). Furthermore, the rate of conversion is invariant when acrylonitrile is added. This rules out the presence of the free radical mechanism in this oxidation reaction. So the ionic reaction is preferred in this oxidation study. Commonly, the enhancement of the electrophilic activity of peroxide will minimize the significance of undesirable free radical methods, resulting in a mixture of products [40]. A literature study [40] reveals that at higher pH the PMS exists as a dianion $(-O-O_3)$ and at lower pH, the oxidant exists as HSO₅⁻ ions. The absorption spectra represent spectral changes, supporting the complex formation.

$$HSO_{5}^{-} \underbrace{K_{1}}_{C_{6}H_{5}CH} = NC_{6}H_{5} + HSO_{5}^{-} \underbrace{k_{2}}_{Slow} [Complex]$$

$$[Complex] \longrightarrow C_{6}H_{5}CHO + C_{6}H_{5}^{+}NH + H_{2}SO_{4}$$

$$2C_{6}H_{5}^{+}NH \xrightarrow{Dimerizes} C_{6}H_{5}N = NC_{6}H_{5} + 2H^{+}$$

Scheme 1 Probable mechanism for the oxidation of aromatic anil by PPMS.

The investigation results illustrate a fascinating note that the increase in H^+ retards the rate of the reaction. With the decrease in pH, the molecule gains a proton, becomes less negatively charged, and hence the rate of the reaction decreases [41]:

$$HSO_5^- \Leftrightarrow SO_5^{2-} + H^+$$

The species HSO_5^{-} is more reactive than SO_5^{2-} species. The higher reactivity of HSO_5^{-} is consistent both with an electrostatic effect and with weakening of the peroxide bond by the proton [42]. Also, in strong acid, the anil exists as a $C_6H_5CH=^+NHC_6H_5$ form. It is observed that when the acid strength is increased, there is a decrease in the rate, which may be due to the less reactive protonated form than nonprotonated form. Based on the stoichiometry of the reaction and above experimental results, the following reactions (Scheme 1) are believed to constitute the most probable mechanism of the reaction. The formation of complex is in agreement with the literature study [43,44], and the intermediate formed is experimentally confirmed at 790 nm (Fig. 3). The next step (decomposition of



Figure 3 UV spectrum showing a probable formation of an intermediate complex in oxidation of aromatic anil by PPMS.

complex) is a slow reaction and is likely to be the ratedetermining step. Simultaneously, at 429 nm, a peak appears and is stable until the end of the reaction, which is the azobenzene product. Based on the above experimental observations, a probable mechanism, shown in Scheme 1, is suggested.

The above mechanism leads to the following rate law:

Rate =
$$-d[KHSO_5]/dt = K_1k_2[anil][KHSO_5]$$

This rate law satisfactorily explains all the experimental results.

Effect of Substituents

The effect of substituents on the rate was studied by varying the substituents H, *m*-CH₃, *p*-OC₂H₅, *p*-OCH₃, *p*-Cl, *m*-Cl, *m*-NO₂, and *p*-NO₂ in one of the ring benzaldehyde (or) aniline and in both at five different temperatures 298, 303, 308, 313, and 318K (Table III); $\Delta H^{\#}$ and $\Delta S^{\#}$ values were calculated from the slope and intercept of the plot ln k_{obs}/T versus 1/*T*, respectively.

Hammett Plot for the Aniline Moiety

Hammett made a unique discovery [45] about the linear free energy relationships for the side chain. The type of concave upward and concave downward curves in the Hammett plot has been reported earlier [46]. The concave downward curve was obtained for the anils with substituents in the aniline moiety (Fig. 4). The electronreleasing substituents fall on the one side of the curve with a positive slope and the electron-withdrawing substituents on the other side with a negative slope. The



Figure 4 Hammett plot for PPMS oxidation of aromatic anils (substitution in the aniline moiety) at 298 K.

Table VReaction Constant for the PPMS Oxidation ofAromatic Anils

Substituent	Temperature (K)	$ ho^+$	$ ho^-$
Aniline moiety	298	1.7342	0.8407
-	303	1.7227	0.7561
	308	1.6063	0.7002
	313	1.4177	0.6981
	318	1.1474	0.3285
Benzaldehyde	298	1.5861	0.7984
moiety	303	1.4723	0.7632
	308	1.3081	0.7406
	313	1.1674	0.5688
	318	0.9896	0.2781
Combination of	298	1.6976	0.8273
aniline and	303	1.3471	0.7946
benzaldehyde	308	1.3555	0.7731
moieties	313	1.2899	0.6522
	318	1.1960	0.5975

isokinetic and Exner plots reveal that there is no change in the reaction mechanism with respect to substituents in the aniline moiety. Para- and metasubstituted anils with substituents in the aniline moiety in aqueous acetic acid at 298-318 K confirm the Exner relationship, also the activation parameters to the isokinetic relationship but not to any of the linear free energy relationships. The isokinetic temperature lies within the experimental range. With the knowledge of substituent constants, it is possible to obtain reaction constants for a wide range of organic reactions. The reaction constant, or sensitivity constant, ρ , describes the susceptibility of the reaction to substituents, compared to the ionization of benzoic acid. It is equivalent to the slope of the Hammett plot. As the value of ρ is related to the charge during the rate-determining step, mechanisms can be devised based on this information. The mechanism for the reaction of an aromatic compound occurs through one of two mechanisms, the compound can be modified with substituents with different ρ values and kinetic measurements taken. Once these measurements have been made, a Hammett plot can be constructed to determine the value of ρ . If one of these mechanisms involves the formation of charge, this can be verified based on the ρ value. The values of ρ^+ and ρ^{-} at five different temperatures are given in Table V (aniline moiety). The unsubstituted anil is the most reactive in this series. But both the electron-releasing and -withdrawing substituents retard the rate of the reaction considerably. The electron attractors can retard the reaction rate only when there is a development of positive charge in the transition state:



Since the electron-releasing substituents also retard the rate of the reaction, the rate-determining step proceeds with the development of negative charge on the nitrogen atom of anil:



It is to be noted that this kind of transition state has been suggested in the oxidation of sulfides by pyridinium chlorochromate (PCC) [47] and pyridinium dichromate (PDC) [48] and anil by isonicotinium dichromate (INDC) [36]. Gurunathan et al. [36] have established the order dependence with respect to the reactants and other kinetic parameters of anils (substitution only in the aniline moiety). The formation of oxalatochromate species is reported as the intermediate of the reaction since oxalic acid is used as a catalyst.

Hammett Plot for the Benzaldehyde Moiety

The concave upward curve was obtained for the anils with substituents in the benzaldehyde moiety (Fig. 5). The electron-releasing substituents fall on the one side of the curve with a negative slope and the electronwithdrawing substituents on the other side with a positive slope. The isokinetic and Exner plots reveal that there is no change in the reaction mechanism with respect to the substituents in the benzaldehyde moiety. The values of ρ^+ and ρ^- at five different temperatures are given in Table V (benzaldehyde moiety). The unsubstituted anil is also the less reactive in this series. But both the electron-releasing and -withdrawing substituents accelarate the rate of the reaction considerably, dissimilar to the aniline moiety. This shows the opposite kind of behavior compared with the aniline moiety.





Hammett Plot for a Combination of Aniline and Benzaldehyde Moieties

The concave upward curve was obtained for the anils with substituents in a combination of aniline and benzaldehyde moiety (Fig. 6), suggesting that the electronreleasing substituents fall on the one side of the curve with a negative slope and the electron-withdrawing substituents on the other side with a positive slope like in substituents only in the benzaldehyde moiety.



Figure 5 Hammett plot for PPMS oxidation of aromatic anils (substitution in the benzaldehyde moiety) at 308 K.



Figure 6 Hammett plot for PPMS oxidation of aromatic anils (substitution in a combination of aniline and benzalde-hyde moieties) at 298 K.

CONCLUSIONS

The reaction followed first-order kinetics with respect to the concentration of [anil], PPMS, and [acid], respectively. Under the experimental conditions, aromatic anil is oxidized to benzaldehyde and azobenzene. The high negative entropy of activation suggested that the formation of a complex is a slow step. The concave downward curve of the Hammett plot was obtained for the anils with substituents in the aniline moiety, whereas the concave upward curve was observed for the substituents in the benzaldehyde moiety and for the substituents in the combination of aniline and benzaldehyde moieties. The oxidation can also be analyzed for special types of drugs.

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