Oxidation of Aromatic Anils in Aniline Moiety by *meta*-Chloroperbenzoic Acid in Aqueous Acitic Medium

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The kinetics of oxidation of aromatic anils in aniline moiety by *meta*-chloroperbenzoic acid (*m*-CPBA) has been studied in aqueous acitic medium. The order of reaction was found to be second order with respect to aromatic anil and first order with respect to *m*-chloroperbenzoic acid. The increase of [H⁺] in this oxidation retards the rate of reaction. The effects of substituents on the oxidation rate were studied with 3 *meta*- and 5 *para*- substituted anils at five different temperatures. Thermodynamic parameters for the oxidation have been determined and discussed. *meta*-Chloroperbenzoic acid oxidation with substituted anils fulfills the isokinetic relationship and Exner relationship but not to any of the linear free energy relationships. The deviation of Hammett plot was noted and a concave downward curve was obtained for the anils with substituents in aniline moiety.

Keywords: Aromatic anils, Kinetics, Aniline moiety, *meta*-Chloroperbenzoic acid.

INTRODUCTION

meta-Chloroperbenzoic acid (*m*-CPBA) is a useful oxidizing reagent for epoxidation of olefins, the Baeyer-Villiger oxidation of ketones and oxidation of amines, sulfides and selenides[1-6]. Since *m*-chloroperbenzoic acid by itself generally can be used for the above oxidations without the aid of promoters (or) catalysts, there are few studies on oxidation with a combined system of *m*-chloroperbenzoic acid and such activators[7,8]. In this paper, we report simple and effective approaches for the selective aromatic anils in aniline moiety using *m*-chloroperbenzoic acid in organic solvents. 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 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 substitutent in the other ring. It is therefore possible to get several reaction constants for different substituents in one of the two rings[9-11]. The kinetics and mechanism of oxidation of some substituted anils, using several oxidants have been reported[9-15]. Literature survey reveals that no report is available on the kinetics of oxidation of *meta*- and *para*- substituted aromatic anils in aniline moiety with *m*-chloroperbenzoic acid. Herein, we would like to report the kinetics and mechanism of oxidation of anils in aniline moiety by *m*-chloroperbenzoic acid.

EXPERIMENTAL

Anils were prepared[9-11,15] by refluxing equimolar quantities of benzaldehyde and aniline (Sigma Aldrich) in ethanol for about 2 to 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. All other chemicals used were of analytical grade (Merck, India). Acetic acid was purified by redistillation. All the reagents were prepared just before the reactions were carried out. A solution of *m*-chloroperbenzoic acid in acetic acid was prepared fresh and standardized iodo-metrically. All the reactions were carried out in a thermostat and the temperature was controlled to ± 0.1 °C. The reactions were performed under pseudo-first order conditions by maintain excess of anil over 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 from log (titre) *versus* time plots. All the rate constants were averages of two or more determinations.

Product analysis: Under kinetic conditions, stoichiometric amounts of the substrate and *m*-chloroperbenzoic acid were mixed.

The reaction mixture solvent ethanol was extracted. The dark brown extract, when subjected to TLC, 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 m.p. and UV-visible spectrum. Formation of the azoben-zene was also confirmed by UV-visible spectra [λ_{max} 429 nm] of the reaction solutions during and after the completion of the reaction. This was in agreement with the literature value[9-11,16]. The λ_{max} of azobenzene was confirmed by comparing with that of the authentic sample in aqueous acetic acid medium.

RESULTS AND DISCUSSION

At fixed concentrations of *m*-chloroperbenzoic acid and H$_2$SO$_4$, the increase in concentration of aromatic anil increases the rate of the reaction. Under the identical experimental conditions [anil] >> [*m*-CPBA], the pseudo-first order linear plot of log (titre) *versus* time is linear upto 80 %, as shown in Fig. 1.
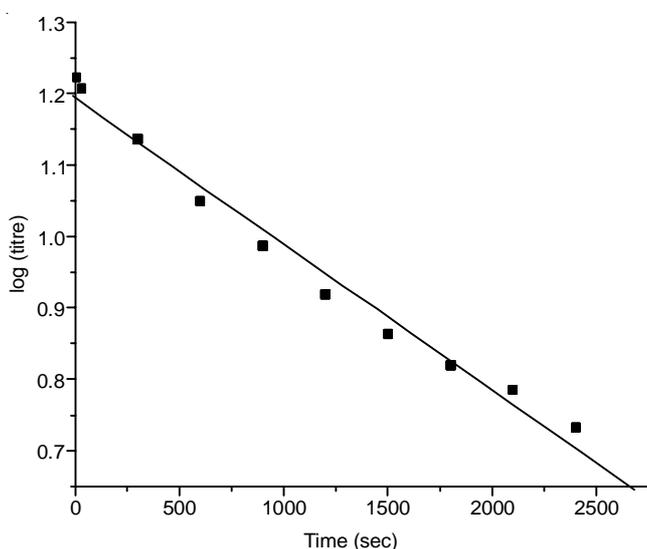
Fig. 1. Pseudo-first order plot for *m*-chloroperbenzoic acid oxidation of aromatic anil at 308 K

The reaction followed second order kinetics with respect to the concentration of anil and is the first order with respect to the concentration of *m*-chloroperbenzoic acid, respectively. The order in [anil] was two, as revealed by the slope of the plot of log k_{obs} against log [anil] (Fig. 2), with correlation coefficient (r = 0.992).

The kinetic order in acidity appears to be unity, but increase in [H$^+$], the rate of the reaction was decreased. The kinetic results are summarized in Table-1.

The ionic strength of the reaction varies by the addition of Na$_2$SO$_4$ and its influence on 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) decreases the rate of the reaction and the rate data are listed in Table-2. Temperature dependence studies were conducted for all the substituted anils (substitution in Y ring separately) between 298 and 318 K.

The rate constants for the reaction systems and activation parameters are evaluated from the Eyring plots as listed in
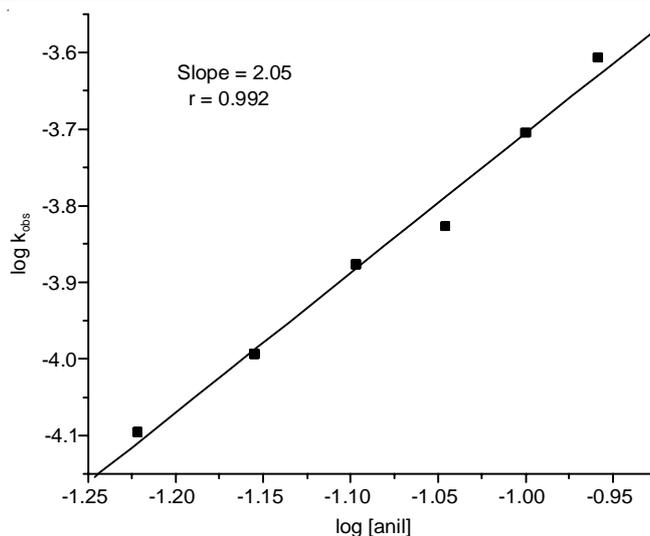
Fig. 2. Plot of log k_{obs} *vs* log [anil] at 308 K

TABLE-1
EFFECT OF VARYING THE CONCENTRATION OF ANIL, *m*-CHLOROPERBENZOIC ACID (*m*-CPBA), AND H$^+$ ON THE RATE AT 308 K

10^2 [Anil] (mol dm^{-3})	10^3 [*m*-CPBA] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	HOAc (%)	10^4 k_{obs} (s^{-1})
6.0	5.0	1.0	50	1.13
7.0	5.0	1.0	50	1.58
8.0	5.0	1.0	50	2.04
9.0	5.0	1.0	50	2.61
10.0	5.0	1.0	50	3.27
8.0	3.0	1.0	50	1.16
8.0	4.0	1.0	50	1.33
8.0	5.0	1.0	50	2.04
8.0	6.0	1.0	50	1.68
8.0	7.0	1.0	50	1.60
8.0	5.0	0.8	50	2.61
8.0	5.0	0.9	50	2.27
8.0	5.0	1.0	50	2.04
8.0	5.0	1.1	50	1.44
8.0	5.0	1.2	50	1.16

TABLE-2
EFFECT OF [Mn(II)], [ACRYLONITRILE] AND [Na$_2$SO$_4$] ON THE REACTION RATE AT 308 K

[Mn(II)] (mol dm^{-3})	[Acrylonitrile] (mol dm^{-3})	[Na$_2$SO$_4$] (mol dm^{-3})	10^4 k_{obs} (s^{-1})
0	-	-	2.04
0.02	-	-	1.77
0.04	-	-	1.58
0.06	-	-	1.40
0.08	-	-	1.19
-	0	-	2.04
-	0.02	-	1.25
-	0.04	-	1.20
-	0.06	-	1.28
-	0.08	-	1.17
-	-	0	2.04
-	-	0.02	1.24
-	-	0.04	1.19
-	-	0.06	1.23
-	-	0.08	1.18

[anil] = 0.08 mol dm^{-3}; [*m*-CPBA] = 0.005 mol dm^{-3}; [H$^+$] = 1 mol dm^{-3}; HOAc-H$_2$O = 50 % (v/v); Temperature = 308 K

TABLE-3
TEMPERATURE EFFECT AND THERMODYNAMIC PARAMETERS OF *m*-CHLOROPERBENZOIC ACID OXIDATION OF ANILS

Moiety	S. No.	Substituents	$10^4 \times k_{obs}$ (s^{-1})					$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J K^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	E_a (kJ mol^{-1}K^{-1})	r	SD
			25 °C	30 °C	35 °C	40 °C	45 °C						
Aniline	1	H	1.75	1.90	2.04	2.28	2.47	11.21	279.42	97.27	13.59	0.994	0.01
	2	*m*-CH$_3$	1.21	1.30	1.53	1.97	2.18	22.48	244.97	97.93	24.86	0.979	0.05
	3	*p*-CH$_3$	0.57	0.89	1.03	1.78	2.02	48.21	164.26	98.80	50.59	0.981	0.10
	4	*p*-OC$_2$H$_5$	0.71	0.96	1.21	1.66	1.95	37.70	197.81	98.63	40.08	0.996	0.03
	5	*p*-OCH$_3$	0.36	0.65	0.91	1.48	1.76	60.55	126.19	99.42	62.93	0.987	0.11
	6	*p*-Cl	1.81	2.10	2.43	2.92	3.23	20.91	246.56	96.85	23.29	0.997	0.01
	7	*m*-Cl	1.36	1.67	1.81	2.29	2.84	25.57	233.40	97.46	27.95	0.986	0.04
	8	*m*-NO$_2$	2.44	2.87	3.64	4.30	5.01	26.49	225.37	95.90	28.87	0.997	0.02
	9	*p*-NO$_2$	0.49	0.91	1.30	2.27	2.68	65.44	107.22	98.46	67.82	0.987	0.12

[Anil] = 0.1 mol dm^{-3}; [*m*-CPBA] = 0.005 mol dm^{-3}; [H$^+$] = 1 mol dm^{-3}; HOAc-H$_2$O = 50 % (v/v)

(Table-3). When an attempt is made to fit in the rate data of *meta*- and *para*- substituted anils in aniline moiety into the Hammett equation, a concave downward curve was obtained for the anils with substituents in the aniline moiety.

Effect of dielectric constant: The rate of the reaction was studied by varying aqueous acetic acid mixtures and by maintaining the concentration of anil, *m*-chloroperbenzoic acid and temperature as constant (Table-4). The results obtained shows that the rate decreases with increase in percentage of acetic acid, *i.e.* with decreasing dielectric constant (D) or polarity of the medium. This directs to the conclusion that there is a charge development in the intermediate state suggesting a polar (ionic) mechanism.

TABLE-4
PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE
OXIDATION OF ANILS BY *m*-CHLOROPERBENZOIC
ACID IN DIFFERENT ACETIC ACID COMPOSITIONS

% Acetic acid	(D)	$10^4 k_{obs}$ (s^{-1})
30	56.83	3.10
40	49.60	2.51
50	42.37	2.04
60	35.14	1.02
70	27.90	0.97

[Anil] = 0.1 mol dm^{-3}; [*m*-CPBA] = 0.005 mol dm^{-3}; [H$^+$] = 1 mol dm^{-3}; Temperature = 308 K

Mechanism: The known fact is that the free radicals can be produced by the homolytic fission of peroxide bond. But the addition of acrylonitrile monomer shows no variation in the reaction rate and no formation of turbidity in the oxidation of aromatic anils[9-11]. This rules out the presence of free radical mechanism in this oxidation reaction. So the ionic reaction is preferred in this oxidation study. Generally, the enhancement of the electrophilic activity of peroxide will minimize the importance of undesirable free radical pathways, resulting in a mixture of products[9-11,17]. The absorption spectra represent spectral changes supporting the complex formation. The investigation results illustrate a fascinating note that the increase of H$^+$ retards the rate of the reaction. With the decrease of pH, the molecule gains a proton, becomes less negatively charged and hence the rate of the reaction decreases[18]. Also in strong acid, the anil exists as C$_6$H$_5$CH = $^+$NHC$_6$H$_5$ form. It is observed that when the acid strength is increased, there is a decrease in the rate which may be due to less protonated form than unprotonated form of anil[9-11].

The literature study[19] reveals that the reaction of anil proceeds through less protonated and unprotonated form of anil and the (increase in H$^+$ increase the reaction rate) less protonated anil is reactive in 3-butyn-2-one. But in the present study increase in H$^+$ leads to the decrease in reaction rate[9-11]. Based on the stoichiometry of the reaction and above experimental results, the following reactions (**Scheme-I**) are believed to constitute the most probable mechanism of the reaction. The formation of complex is in agreement with the literature study[9-12,19,20] and the intermediate formed is experimentally confirmed at 790 nm (Fig. 3). Decomposition of complex is a slow reaction and is likely to be the rate determining step. The results can be explained by the formation of intermediate complex. Usually peroxy ions act as strong nucleophiles. Simultaneously, at 429 nm, a peak appears and is stable till the end of the reaction, which is the azobenzene product[8-11]. Based on the above experimental observations, a probable mechanism, shown in **Scheme-I** is suggested.
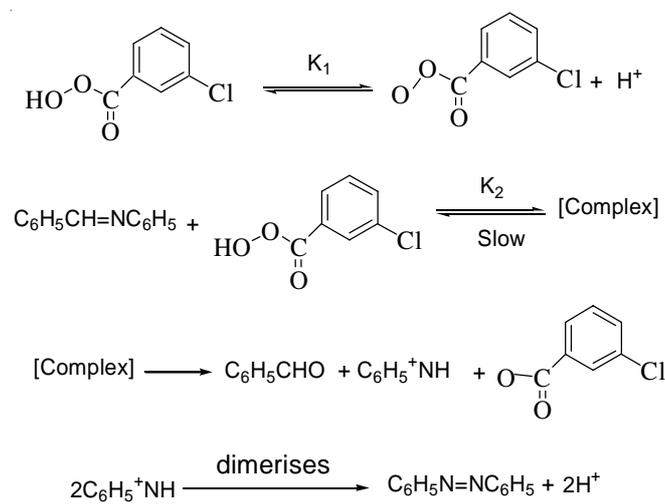
Scheme-I: Probable mechanism for the oxidation of aromatic anil by *m*-chloroperbenzoic acid

The above mechanism leads to the following rate law:
        Rate = -d[*m*-CPBA]/dt = K$_1$k$_2$[anil] [*m*-CPBA]
This rate law satisfactory explains all the experimental results.

Effect of substituents on the reaction rate: The kinetics and oxidation of anil and *m*-CH$_3$, *p*-CH$_3$, *p*-OC$_2$H$_5$, *p*-OCH$_3$, *p*-Cl, *m*-Cl, *m*-NO$_2$, *p*-NO$_2$ anils were conducted under pseudo-
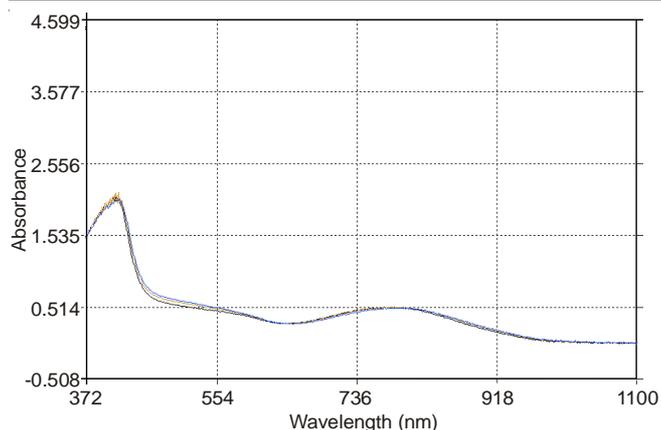
Fig. 3. UV spectrum showing a probable formation of intermediate complex in oxidation of aromatic anil by *m*-chloroperbenzoic acid

first order conditions at five different temperatures 298, 303, 308, 313 and 318 K to determine various thermodynamics parameters. The analysis of the data in the Table-3 indicates that the oxidation is neither isoenthalphic nor isoentropic but confirms with isokinetic relationship of compensation law. Since the reactions are of ion-polar, it is expected that the entropy of the activated complex for all the anils should be nearly the same order of magnitude. The thermodynamics parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$ values are calculated from the slope and intercept of the plot ln k_{obs}/T *versus* 1/T, respectively (Fig. 4). The effect of substituents on the rate is studied by varying the substituents H, *m*-CH$_3$, *p*-CH$_3$, *p*-OC$_2$H$_5$, *p*-OCH$_3$, *p*-Cl, *m*-Cl, *m*-NO$_2$ and *p*-NO$_2$ in one of the rings benzaldehyde (or) aniline.
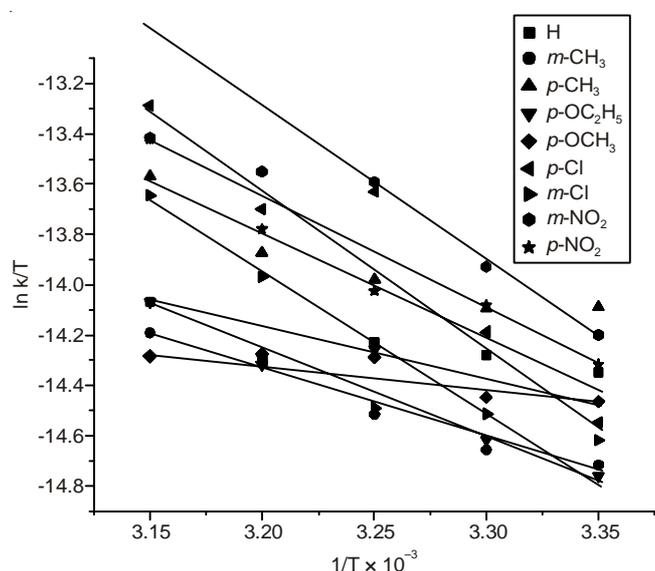
Fig. 4. Eyring's plot for *m*-chloroperbenzoic acid oxidation of anils in aniline moiety at 308 K

Hammett relationship/Hammett plot for aniline moiety: Hammett made a unique discovery[21] about the linear free energy relationships for the side chain. Application of the Hammett equation with the usual substituent constant σ to the log k_{obs} data of the *meta*- and *para*- substituted aromatic anils resulted in a concave downward curve (Fig. 5). Similar types of Hammett plots were observed previously in some reaction
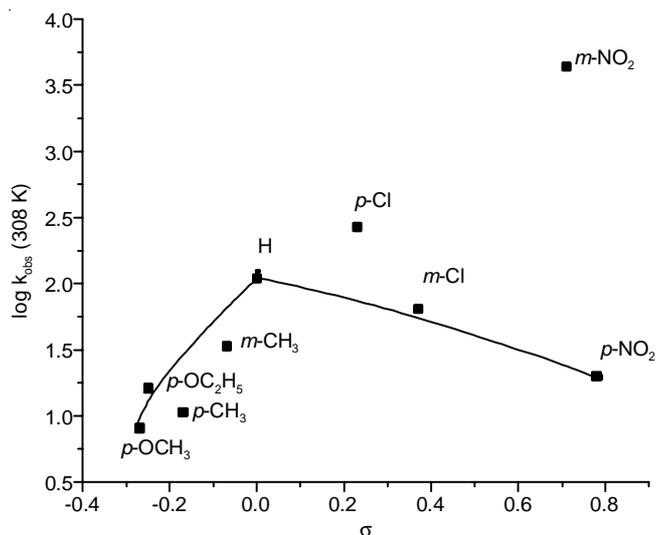
Fig. 5. Hammett plot for *m*-chloroperbenzoic acid oxidation of aromatic anils in aniline moiety at 308 K

kinetics[9-11,22]. The concave downward curve was obtained for the anils with substituents in aniline moiety. The electron-releasing 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 isokinetic plot and Exner plot reveal that there is no change in reaction mechanism with respect to substituents in aniline moiety. *para*- and *meta*-substituted anils with substituents in 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.

Isokinetic temperature is the temperature at which all the compounds react at same speed since this temperature variation of substituent has no influence on the free energy of activation. In an isoentropic oxidation, the isokinetic temperature lies at infinite and only enthalpy of activation determines the reactivity. The isokinetic temperature is zero for an isoenthalphic series and the reactivity is determined by the entropy of activation[23].

$$\Delta H^{\#} = \Delta H^{\circ} + \beta \, \Delta S^{\#}$$

β is the isokinetic temperature and found to be 333 K which is greater than the experimental temperature.

The values of free energy of activation of the reactions were found to be more or less similar. This is due to the fact that at isokinetic temperature the change of substituent has no influence on the free energy of activation. If the isokinetic temperature is infinite in isoentropic oxidation reactions, only the enthalpy of activation finalizes the reactivity and if the isokinetic temperature is zero in isoenthalpic oxidation reactions, only the entropy of activation finalizes the reactivity[24]. The values of the negative and positive ρ values, ρ^{+} and ρ^{-}, respectively, at different temperature are given in Table-5.

The unsubstituted anil is the most reactive in this series. 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 anil by INDC[15]. Venkatesh and Karunakaran[9-11] have established the order dependence with respect to the reactants and other kinetic parameters of anils (substitution in

TABLE-5
REACTION CONSTANT FOR THE *m*-CHLOROPERBENZOIC
ACID OXIDATION OF AROMATIC ANILS

Substitutents	Temperature (K)	ρ^+	ρ^-
Aniline moiety	298	4.52	0.57
	303	3.88	0.23
	308	3.55	0.31
	313	2.58	0.26
	318	2.21	0.11

aniline moiety, benzaldehyde moiety and also combination of aniline and benzaldehyde moieties). The formation of oxalatochromate species is reported as the intermediate of the reaction since oxalic acid is used as catalyst.

Conclusion

Concave downward curve of Hammett plot was obtained for the anils with substituents in the aniline moiety. The electron-releasing 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 isokinetic plot and Exner plot reveal that there is no change in reaction mechanism with respect to substituents in aniline moiety.

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