Lack of Linear Free Energy Relationship: Tungsten(VI) Catalyzed Perborate Oxidation of Anilines

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Received 20 July 1998; accepted 26 March 1999

ABSTRACT: The rates of tungsten(VI) catalyzed perborate oxidation of 29 para-, meta- and ortho-substituted anilines in aqueous acetic acid at 35–55°C conform to the Exner relationship, also the activation parameters to the isokinetic relationship but not to any of the linear free energy relationships. The results are rationalized. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 571–575, 1999

INTRODUCTION

Sodium perborate, $NaBO_3.4H_2O$, is a cheap, eco-friendly, large-scale industrial chemical, primarily used in detergents as a bleaching agent. It is a mild oxidant and in glacial acetic acid effectively oxidizes aniline, present in excess, to azobenzene [1,2]. In aqueous acetic acid the oxidation is sluggish but tungsten(VI) catalyzes the same. The catalyzed oxidation is zero, first and second order in the oxidant, catalyst, and substrate, respectively [3]. Hydrogen peroxide is the reactive species of perborate [4]. Rapid generation of dioxoperoxotungsten(VI) followed by its stabilization by aniline, present in swamping excess as (aniline)dioxoperoxotungsten(VI), which acts as the oxidizing agent and transfers oxygen to molecular aniline in a rate-limiting step is the probable mechanism of oxidation [3]. This article reports absence of well-defined substituents effect; the oxidation rates of 29 para-, meta- and ortho-substituted anilines do not conform to any of the linear free energy relationships.

Generally, the oxidation of aniline involves either (a) rate-determining oxygen transfer from the oxidant to the substrate resulting in the formation of aniline oxide or phenylhydroxylamine which reacts with another molecule of aniline in a fast step to give the product or (b) rate-limiting abstraction of hydride ion from molecular aniline by the oxidant, followed by the fast reaction of $PhNH^+$ with aniline to yield the product. Kinetics of oxidation of anilines by a variety of oxidants have been reported and they conform to the Hammett equation (reaction constant: ρ) or the modified Hammett equation (reaction constant: ρ^-) or the Brown-Okamoto equation (reaction constant: ρ^+). The oxidation by chloramine-T (aqueous ethanol, $[OH^-] = 0.10$ mol dm^{-3}, $\rho = -1.0$) [5], peroxodisulfate (aqueous 2-propanol, $[OH^-] = 0.48$ mol dm^{-3}, $\rho = -1.3$) [6], (aqueous t-butanol, $[OH^-] = 0.25$ mol dm^{-3}, $\rho = -1.48$) [7], carbonate radical (pH 8.5, $\rho^+ = -1.0$) [8], borate radical (pH 11.4, $\rho^+ = -0.87$) [9] and hexacyanoferrate(III) (aqueous ethanol, $10^2 [OH^-] = 2.5$ mol dm^{-3}, $\rho^+ = -4.1$) [10] were studied in basic medium and that by N-bromoacetamide (aqueous methanol, $\rho = -0.79$) [11], periodate (aqueous methanol, $\rho = -2.44$) [12], peroxodisulfate (aqueous ethanol, $\rho^+ = -1.41$) [13], peroxomonophosphoric acid (aqueous acetonitrile, pH 5.4, $\rho = -1.37$, $\rho^+ = -1.31$, $\rho^- = -1.38$) [14], peracetic acid (ethanol, $\rho = -1.86$) [15] and lead(IV) acetate

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CCC 0538-8066/99/080571-05

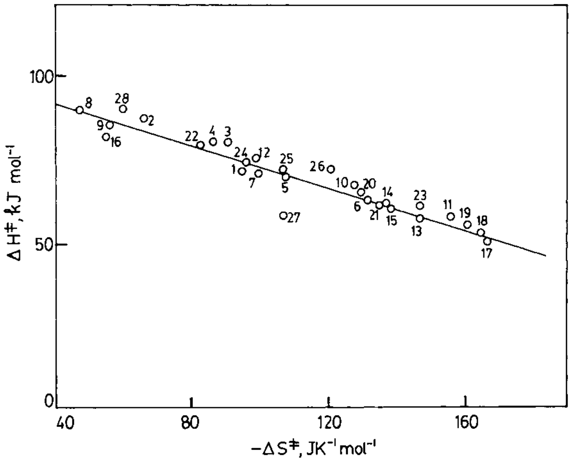

Figure 1 The Isokinetic Plot. The numbers correspond to substituents as given in Table I.

(chloroform-acetic anhydride, $\rho = -2.4$) [16] at neutral pH. Similar studies in acidic medium include chloramine-T (aqueous acetic acid, $10^2[HClO_4] = 0.62 - 5.0$ mol dm^{-3}) [17], N-chlorosuccinimide (acetic acid, $\rho = -1.5$) [18], bromate ion (aqueous acetic acid, $\rho = 1.74$) [19], iodate catalyzed by ruthenium(III) (aqueous acetic acid, $10^2[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -2.8$) [20], periodate (aqueous acetic acid, $\rho^+ = -2.3$) [21], peroxodisulfate (aqueous acetic acid, $\rho = 1.88$) [22], thallium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -3.0$) [23], thallium(III) catalyzed by ruthenium(III) (aqueous acetic acid, $[HClO_4] = 1.0$ mol dm^{-3}, $\rho = -0.76$) [23], iron(III)-bipyridyl complex (aqueous methanol, $10^2[HClO_4] = 1.2$ mol dm^{-3}, $\rho^+ = -3.10$) [24] and pyridinium chlorochromate (chlorobenzene-nitrobenzene, 10^3 $[Cl_2CHCOOH] = 3 \pm 0.5$ mol dm^{-3}, $\rho^- = -3.75$) [25].

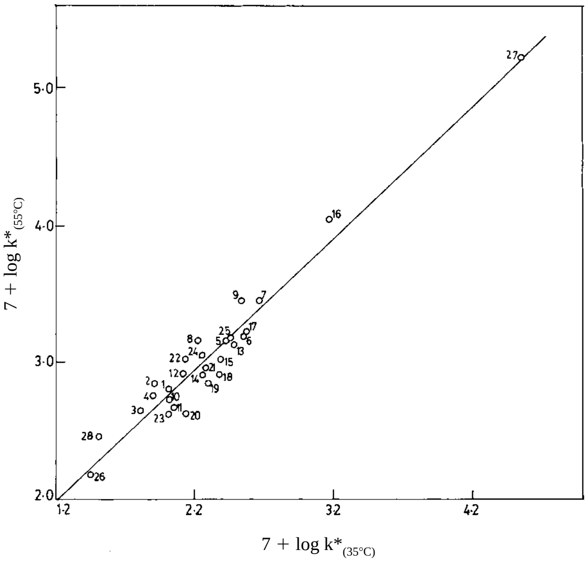

Figure 2 The Exner Plot. The numbers are as in Table I.

EXPERIMENTAL

Sodium perborate was used as received. Anilines were redistilled or recrystallized before use. All chemicals were of analytical grade. Aqueous solution of perborate was prepared afresh and standardized iodometrically. Kinetic studies were made under pseudo-first-order conditions with catalytic concentration of tungsten(VI) and large excess of anilines in aqueous acetic acid [3]. Sodium tungstate was used as the catalyst. The progress of the oxidation was followed up to about 80% completion by iodometric estimation of the unconsumed oxidant at different reaction time and the temperature was controlled to ±0.1°C. The oxidation rates were found from the least squares slopes of the linear plots of [oxidant] versus time. The oxidation is sluggish below 35°C and above 55°C evaporation of solvent (water) occurs; the kinetic study was restricted to 35–55°C. In all the cases, formation of the corresponding substituted azobenzene was confirmed by UV-visible spectra of the reaction solutions during and after completion of the oxidation.

RESULTS AND DISCUSSION

Operation of linear free energy relationships in tungsten(VI) catalyzed perborate oxidation was studied with 29 para-, meta- and ortho-substituted anilines. The activation parameters were calculated from $k^*(= \text{rate}/[\text{substrate}]^2)$ at 35, 40, 45, 50, and 55°C using the Eyring relationship by the method of least squares (Table I). The oxidation is not isoentropic; in an isoentropic series only enthalpy of activation determines the reactivity and the isokinetic temperature (β) is at infinity [26]. At the isokinetic temperature all the compounds of the reaction series react at equal rate; the variation of substituent at this temperature has no influence on the free energy of activation. Transgressing the isokinetic temperature results in the reversal of the order of reactivities. The title reaction is neither isoenthalpic. Only activation entropy determines the reactivity in an isoenthalpic series, the isokinetic temperature is zero. On the other hand, compensation law, also known as isokinetic relationship, exists. It is the linear relationship between enthalpy of activation and entropy of activation (Fig. 1., correlation coefficient, $r = 0.957$; standard deviation, $sd = 3.36$; number of data sets, $n = 28$; *o*-phenylenediamine is excluded). The maximum possible errors in activation enthalpy (δ) and activation entropy are 3.4 kJ mol^{-1} and 11.2 J K^{-1} mol^{-1}, respectively. The error criterion is satisfied in the present study, that is, $\Delta\Delta H^{\#} \gg 2\delta$ and hence the correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ is significant. However, this relationship is to be viewed with scepticism as these parameters are mutually interdependent [27,28]. But existence of Exner relationship, the linear double logarithmic relationship between rates at two different temperatures, confirms the isokinetic relationship and reveals that all the anilines are oxidized through a common mechanism (Fig. 2., $r = 0.976$, $sd = 0.122$, $n = 28$). The isokinetic temperature is -1197 K. There is no general theory which excludes negative values of isokinetic temperature [26,29,30]. Also, negative value of isokinetic temperature is not unknown [26]; the isokinetic temperature of peroxodisulfate oxidation of ortho-

Table I Tungsten(IV) Catalyzed Perborate Oxidation of Para-, Meta-, and Ortho-Substituted Anilines[x]

	10^5 k* dm^{-3} mol^{-1} s^{-1}						
No Substituent	35°C	40°C	45°C	50°C	55°C	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}
1. H	1.04	1.3	2.42	3.85	6.24	70.7	95.3
2. *p*-CH_3	0.80	1.17	1.99	2.87	7.12	85.6	65.8
3. *p*-OCH_3	0.66	1.1	1.5	2.94	4.48	78.1	91.2
4. *p*-OC_2H_5	0.81	1.24	1.84	3.16	5.72	78.8	87.5
5. *p-Cl*	2.7	3.9	5.64	9.44	14.8	69.4	108
6. *p*-Br	3.6	5.04	7.4	11.8	15.9	61.5	131
7. *p*-COOH[a]	4.67	8.3	11.4	14.6	31.0	70.3	99.6
8. *p*-$NHCOCH_3$	1.7	2.72	5.6	8.96	14.4	89.2	47.0
9. *p*-NO_2[b]	3.55	6.92	16.3	18.9	28.0	84.1	56.3
10. *p*-$COOC_2H_5$	1.04	1.58	2.32	3.4	5.44	65.7	128
11. *p*-$COCH_3$	1.11	1.66	2.25	3.18	4.68	56.6	156
12. *m*-CH_3	1.28	2.17	3.5	5.16	8.1	73.8	98.9
13. *m*-OCH_3	3.0	5.6	6.92	8.1	13.9	56.8	147
14. *m*-Cl	1.84	2.78	4.4	6.24	8.24	61.2	137
15. *m*-Br	2.44	3.46	5.52	7.84	10.5	60.4	37.5
16. *m*-COOH[b]	14.7	21.3	38.6	57.5	110	81.4	54.9
17. *m*-NO_2[a]	3.62	4.43	5.25	8.83	12.4	50.4	168
18. *m*-$COCH_3$	2.4	2.6	3.83	5.92	8.2	52.2	165
19. *m*, *p*-Cl_2	1.97	2.71	4.0	6.12	7.04	53.6	161
20. *o*-CH_3	1.38	2.13	3.29	4.56	6.8	64.0	130
21. *o*-OCH_3	1.93	3.26	5.68	6.0	9.44	61.1	136
22. *o*-OC_2H_5	1.42	2.51	4.56	5.2	10.8	78.4	83.3
23. *o*-Cl	1.03	1.58	2.31	3.45	4.4	59.7	147
24. *o*-Br[a]	1.8	3.36	5.84	7.55	11.5	73.2	97.5
25. *o*-COOH	2.78	3.69	5.8	10.4	14.6	69.6	107
26. *o*-NO_2	0.29	0.38	0.64	1.1	1.53	71.3	121
27. *o*-OH[c]	364	442	564	820	1610	57.4	107
28. *o*-$COCH_3$	0.34	0.60	1.46	1.89	2.88	89.2	59.9
29. *o*-NH_2[d]	19.5[e]	86.8[f]	274[g]			102	25.9

[x] $10[\text{Aniline}]_0 = 5.0$ mol dm^{-3},
$10^2[\text{Perborate}]_0 = 1.0$ mol dm^{-3},
$10^3[\text{W(VI)}] = 1.0$ mol dm^{-3},

Medium: 50% (v/v) aq. HOAc.

[a] $10[\text{Aniline}]_0 = 2.5$ mol dm^{-3}.
[b] $10[\text{Aniline}]_0 = 1.0$ mol dm^{-3}.
[c] $10^2[\text{Aniline}]_0 = 6.0$ mol dm^{-3}.

$$k^* = \frac{\text{Rate}}{[\text{Aniline}]_0^2}$$

[d] $10^2[\text{Aniline}]_0 = 5.0$ mol dm^{-3},
$10^3[\text{Perborate}]_0 = 5.0$ mol dm^{-3},
$10^4[\text{W(VI)}] = 5.0$ mol dm^{-3}.

[e] 25°C. [f] 35°C. [g] 45°C.

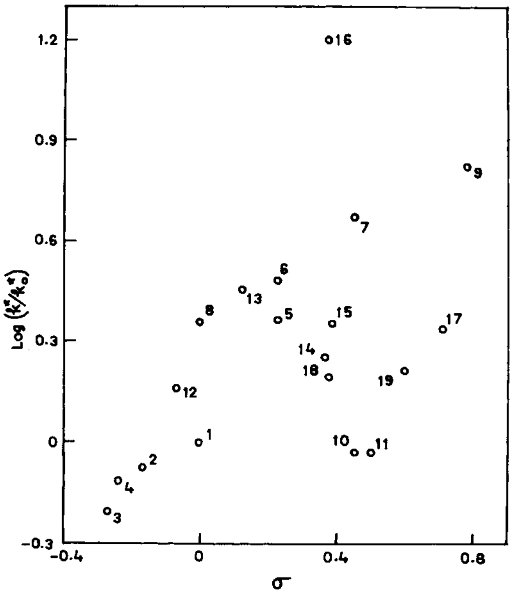

Figure 3 The Hammett Plot. The numbers are as in Table I.

substituted N,N-dimethylanilines is − 893 K [31]. Anomalous behavior of one or two substituents of very high or very low reactivity (points at the extremes of the Exner plot and here it is *o*-aminophenol) may lead to error is slope and hence in isokinetic temperature. Also, current views do not attach much significance to the isokinetic temperature though linear correlation is usually a necessary condition for the validity of the Hammett equation [26–30].

The rates of tungsten(VI) catalyzed oxidation of anilines do not conform to the usual Hammett equation at any of the temperatures studied (e.g., Fig. 3). In anilines the reaction site may conjugate with the para-substituent but correlation of the oxidation rates of para- and meta-substituted anilines separately with any of the single parameters (para: σ, σ_p^+, σ_p^-; meta: σ, σ_m^+) was also unsuccessful. The rate data at all the temperatures studied were analyzed using biparametric equations (para: σ_I & σ_R, σ_I & σ_R^-, σ_I & σ_R^+, F & R; meta: σ_I & σ_R, σ_I & σ_R^-, σ_I & σ_R^+, F & R) but with failure. As the oxidation is second order with respect to the substrate σ & σ^2 were also employed as explanatory variables but without success [32]. The operation of triparametric equations is possible in reactions which are second order in substrate but no such equation (para: σ_I, σ_R & σ_R^+; σ_I, σ_R & σ_R^-; σ_I, σ_R^+ & σ_R^-; meta: σ_I, σ_R & σ_R^+; σ_I, σ_R & σ_R^-; σ_I, σ_R^+ & σ_R^-) explains the substituents effect. The ortho-substituted anilines also fail to conform to any of the triparametric equations; one of the parameters being the steric susceptibility constant, υ.

Operation of inductive and resonance effects opposing each other is known but the present study has no parallels [32]. The less pronounced substituents effect on the oxidation rate may be explained by the 'compensation effect'. The oxidation involves two aniline molecules in the rate-determining step [3]; the catalyst-aniline complex is likely to be the electrophile and the free aniline is the nucleophile. The influence of the substituent on the reactivity of the nucleophile is approximately compensated by the influence of the same substituent on the reactivity of the electrophile. As exact compensation is unlikely, especially in some of the substituted anilines, the resultant effect is experienced on the oxidation rate.

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