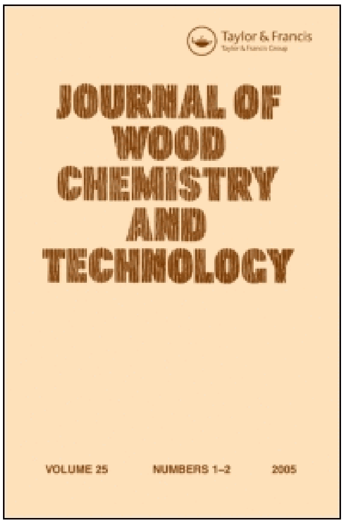

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HIGH CATALYTIC ACTIVITY OF ROSINDONE AND RELATED COMPOUNDS IN ALKALINE PULPING

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ABSTRACT

The efficacies of phenazine, phenazone and rosindone derivatives as additives in alkaline pulping were investigated and compared. Phenazones and rosindones are superior to the phenazines described earlier. Equimolar charges of rosindone sulfonate stabilize carbohydrates more than anthraquinone ($v_M \sim 1.1$) but the delignification effect is slightly inferior ($r_M = 0.72$). Due to low solubility rosindone does not follow the square root relationship. Low rosindone charges ($<0.1\%$) catalyze delignification as efficiently as anthraquinone ($r_M \sim 1$).

The half-wave potentials (pH 14, 90°C, 1N NaOH, SCE, in the presence of wood) were measured. No correlation is to be found between pulping efficacies (r_M-value) and redox potentials ($E_{1/2}$). The differences of the pulping efficacies are mainly explained in terms of chemical stability.

INTRODUCTION

Since the discovery of quinoid redox catalysts for alkaline pulping[1-3] many additional but inferior additives have been reported[4-8]. Fleming[6, 8] and Eckert[7] revealed the activity of N-heterocyclic compounds. Presently phenazine represents the most efficient accelerator within this chemical family. Its efficacy is about a seventh of that of anthraquinone. In this paper we report the activities of N-heterocyclic compounds which are related to phenazine. The phenazones, and especially the rosindones, are significantly more effective than phenazine. Among rosindones redox catalysts as active as anthraquinone are found.

METHOD

A previously described method[9] was used to measure the efficacy of additives. This method, based on the fact that the efficacy of an additive is proportional to the square root of its charge, yields two parameters: r_o describes the efficacy on delignification, v_o is a measure for the carbohydrate stabilization (AQ: $r_o = v_o = 1$). These process-independent parameters permit comparison of different additives based on equal weight percentages. For the comparison of physicochemical properties we define r_M- and v_M-values which refer to the efficacy of an additive of which the charge is given in molar units.

$$r_M = r_o\sqrt{\frac{M}{M_{AQ}}}$$

$$v_M = v_o\sqrt{\frac{M}{M_{AQ}}}$$

M	molecular weight
M_{AQ}	molecular weight of AQ (= 208)

By definition the r_M- and v_M-values of anthraquinone (AQ) are equal to unity.

RESULTS AND DISCUSSION

The pulping results are summarized in tables 1-4. Four replicate standard cooks (AQ) were performed whereas additive cooks were made in duplicate. The experimental results in tables 1-4 are average values. To secure identical experimental conditions, pulps within the same series were cooked simultaneously (for experimental details see ref. 9). The r- and v- values are also given in the table. Some correlation coefficients, the measure

TABLE 1

Results of Phenazines

Additive	Experimental results				Regression		
	Charge % a)	Cl b)	Y % c)	C % d)		SE e)	Corr. coeff. f)
g) AQ	0.09	8.02	51.94	48.19	r_o=0.37	.02	.989
I	0.16	10.96	52.46	47.29	v_o=0.17	.10	.975
I	0.36	8.95	51.64	47.48			
I	0.64	7.99	51.29	47.60	r_M=0.34		
I	1.00	7.36	51.05	47.67	v_M=0.16		
AQ	0.09	7.36	49.90	46.59	r_o=0.11	.01	.960
II	0.04	15.06	53.17	45.96	v_o=0.22	.13	.949
II	0.16	14.36	53.01	46.16			
II	0.36	12.58	52.10	46.20	r_M=0.11		
II	0.64	12.36	52.07	46.28	v_M=0.23		
AQ	0.09	7.33	50.32	47.00			
III	0.04	14.86	53.67	46.49	r_o=0.18	.02	.982
III	0.16	13.51	52.34	45.98	v_o=(0.13)	.79	.329
III	0.36	12.16	52.08	45.38			
III	0.64	10.31	51.35	46.59	r_M=0.20		
AQ	0.09	8.51	48.46	44.75			
IV	0.04	19.00	52.76	43.74	r_o=0.04	.01	.943
IV	0.16	17.71	52.23	43.91	v_o=(0.28)	.09	.779
IV	0.36	17.58	51.99	43.76			
IV	0.64	17.03	52.74	44.66	r_M=0.05		

a) per o.d. wood; b) chlorine number[23]; c) total yield per o.d. wood; d) ligninfree yield per o.d. wood determined as[24] C = Y(1-0.009 Cl); e) SE = standard deviation; f) correlation coefficient as R^2; g) Results of one section refer to one series of cooks performed simultaneously (identical conditions, see ref. 9)

for the quality of the square root fit, of the plot with the lignin-free yields (measure for carbohydrate stabilization, v_o) are low due to high scatter in the yield data. The corresponding v_o-values given in brackets indicate that the value represents only

TABLE 2

Results of Phenazones (cf. Footnotes Table 1)

Additive	Experimental results				Regression		
	Charge %	Cl	Y %	C %		SE	Corr. coeff.
AQ	0.04	8.76	50.01	46.07	r_o=0.25	.01	.999
V	0.16	11.96	51.60	46.05	v_o=0.55	.10	.981
V	0.36	10.05	51.51	46.85			
V	0.64	8.86	51.48	47.37	r_M=0.26		
V	1.00	7.67	51.23	47.69	v_M=0.57		
AQ	0.09	7.52	50.10	46.71			
VI	0.04	11.79	51.62	46.14	r_o=0.43	.04	.971
VI	0.16	9.03	50.58	46.47	v_o=(0.18)	.16	.572
VI	0.36	7.67	49.85	46.41			
VI	0.64	7.29	49.63	46.37	r_M=0.50		
AQ	0.09	8.65	48.72	44.93	r_o=0.49	.05	.978
VII	0.04	13.54	50.33	44.20	v_o=0.54	.11	.982
VII	0.16	9.67	49.02	44.75			
VII	0.36	8.61	48.69	44.92	r_M=0.55		
VII	0.64	7.68	48.77	45.40	v_M=0.60		
AQ	0.09	6.97	46.39	43.48			
VIII	0.04	10.52	47.49	42.99	r_o=0.34	.10	.957
VIII	0.16	9.19	47.36	43.44	v_o=(0.33)	.36	.558
VIII	0.36	7.60	46.20	43.04			
VIII	0.64	7.53	46.68	43.52	r_M=0.42		

a rough estimation. The v_M-values corresponding to such experiments have not been calculated.

The half-wave potentials $E_{1/2}$ of the additives were measured in 1N NaOH at 90°C in presence of wood. The potentials versus SCE are given with the structures. Figure 1 shows that $E_{1/2}$ does not correlate with the delignification efficacy of an additive (r_M). From our experience with about 50 tested additives we conclude that a redox catalyst for alkaline pulping requires a half-wave poten-

TABLE 3

Results of Rosindones (cf. Footnotes Table 1)

Additive	Experimental results				Regression		
	Charge %	Cl	Y %	C %		SE	Corr. coeff.
AQ	0.16	8.49	49.19	45.43	$r_o=0.53$ $v_o=0.74$	.06 .13	.992 .997
IX	0.0625	14.74	51.71	44.85			
IX	0.25	10.17	50.00	45.42			
IX	0.5625	8.38	49.56	45.82	$r_M=0.73$ $v_M=1.03$		
IX	1.0	7.29	49.54	46.29			
AQ	0.04	10.41	51.43	46.61	$r_o=0.51$ $v_o=0.90$	.04 .36	.990 .943
IX	0.04	13.74	53.10	46.54			
IX	0.16	10.18	51.61	46.88			
IX	0.36	8.11	51.38	47.63	$r_M=0.71$ $v_M=1.25$		
IX	0.64	7.35	50.99	47.62			
AQ	0.04	9.26	50.40	46.20	square root relationship not fulfilled		
X	0.16	8.41	49.85	46.08			
X	0.36	8.36	50.07	46.30			
X	0.64	7.79	49.75	46.26			
X	1.00	8.30	50.32	46.56			
AQ	0.01	12.45	50.52	44.86			
-	-	16.86	51.86	43.99	$r_o \sim 0.82$ $r_M \sim 1.02$		
X	0.01	13.07	49.67	43.83			
AQ	0.04	9.44	50.70	46.39	$r_o=0.78$ $v_o=(0.79)$	.05 .36	.982 .643
X	0.04	10.10	50.97	46.34			
X	0.09	8.88	50.52	46.48			
X	0.16	8.38	50.22	46.43	$r_M=0.97$		

tial $E_{1/2}$ (pH 14) in the range between about -550 and -1050 mV. Once this requirement is fulfilled, properties such as xylophilicity[10], chemical stability, solubility[11] etc. are more decisive for the efficacy.

Table 1 contains the results of the phenazine derivatives, table 2 refers to the phenazones, table 3 to the rosindones and table 4 to rosindones in their reduced form.

TABLE 4

Results of reduced Rosindones (cf. Footnotes Table 1)

Additive	Experimental results				Regression		
	Charge %	Cl	Y %	C %		SE	Corr. coeff.
AQ	0.16	6.12	48.97	46.27			
XI	0.04	9.47	49.78	45.54	r_o=0.50	.05	.893
XI	0.16	7.12	48.78	45.65	v_o=(0.39)	.14	.609
XI	0.36	6.39	49.14	46.31			
XI	0.64	6.47	48.69	45.85	r_M=0.67		
AQ	0.16	6.34	49.34	46.52			
XII	0.04	10.31	50.55	45.86	r_o=0.49	.03	.962
XII	0.16	7.90	49.41	45.90	v_o=(0.53)	.24	.653
XII	0.36	6.94	49.97	46.85			
XII	0.64	6.63	49.26	46.32	r_M=0.69		

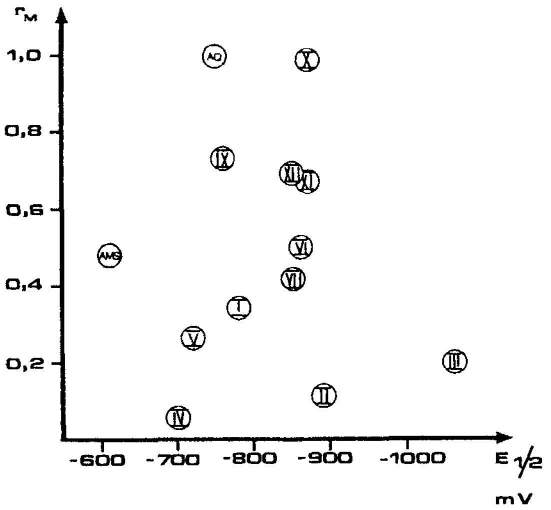
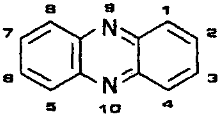
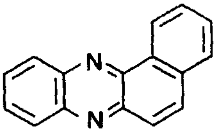


FIGURE 1: Redox potential (90°C, pH 14,1 N NaOH, wood) vs. efficacy on delignification



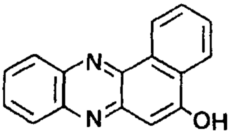
I

$E_{1/2}$ = -780 mV
vs. SCE in 1 N NaOH/90°C



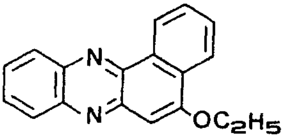
II

$E_{1/2}$ = -890 mV



III

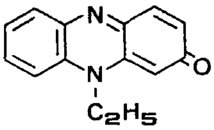
$E_{1/2}$ = -1060 mV



IV

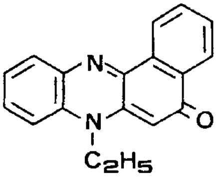
$E_{1/2}$ = -700 mV

An additional annulated benzene ring at position 1 and 2 decreases the efficacy of phenazine (cf. I and II) but increases the activity of phenazone (cf. V and VI). This behaviour compares favourably with the estimated reactivity sequence of these compounds toward nucleophilic attack which is expected to limit their chemical stability under pulping conditions. Utilizing the HMO theory, nucleophilic atom localization energies[12], A^+, have been calculated for all relevant positions of molecules under scrutiny. The smallest value obtained for a given molecule, A^+_{min}, corresponds to the most reactive site and can be taken as a measure for its chemical stability in a nucleophilic environment. Comparing phenazine I (A^+_{min} = 2.118 β) with benzophenazine II (2.083 β) and phenazone V (1.945 β) with benzophenazone VI (2.027 β) it is obvious that appending a benzene ring decreases the stability in the former case and increases it in the latter. The quoted figures are given in units of the adjustable resonance integral β and have been calculated with a parameter set descri-



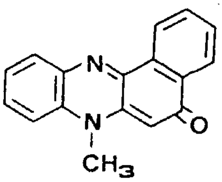
V

$E_{1/2}$ = -720 mV



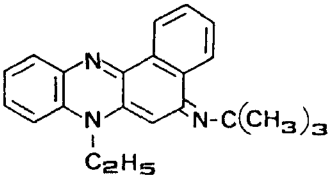
VI

$E_{1/2}$ = -860 mV



VII

$E_{1/2}$ = - 820 mV



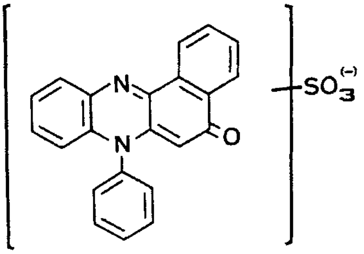
VIII

$E_{1/2}$ = -850 mV

bed elsewhere[13]. In the above consideration only molecules with the same kind of heteroatoms have been compared, which is justified. With structures containing widely differing heteroatoms, such comparisons are less meaningful due to limitations of the simple Hückel approach and therefore no attempt should be made to compare the reactivities of phenazines with those of the phenazones.

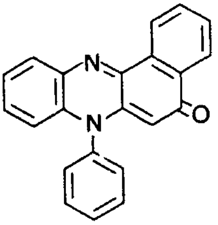
Position 4 of the benzophenazones is still available for nucleophilic attack. Introducing a phenyl ring on the nitrogen at position 10 presumably protects position 4 partially by steric hindrance and therefore enhances the chemical stability. The additional phenyl ring might also increase the xylophilicity[10]. This may explain the superior efficacy of rosindones.

Compounds XI and XII are reduced rosindones in their acetylated form. We assume that they are saponified under alkaline pulping conditions. The activities of XI and XII indicate the mechanism of rosindones to be a cyclic redox one as shown for



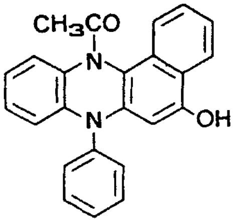
IX

$E_{1/2} = -760$ mV



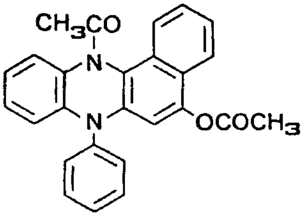
X

$E_{1/2} = -870$ mV



XI

$E_{1/2} = -860$ mV



XII

$E_{1/2} = -850$ mV

anthraquinone[14,15]. The lower efficacy of XI and XII compared to X may be explained by the preceding saponification which might be slow. Note that under strong alkaline conditions hydrolysis at position 3 yields an anion. This decreases the rate of a saponification for the N-acetyl group.

Using equimolar charges rosindone sulfonate (IX) stabilizes carbohydrates more efficiently than anthraquinone ($v_M > 1$). The efficacy on delignification though somewhat inferior to that of AQ, is about 4.6-fold that of phenazine and it is increased by a factor of 2.3 compared to anthraquinone-2-sulfonate (AMS) (compare the ratio of the r_M^2's). For the case of AMS the inferior efficacy versus AQ can be entirely explained by increased hydrophilicity due to the sulfo group[10]. Leaving out the sulfo group in IX to yield rosindone X does not result in such a marked enhancement

(AQ is ∿7 times more efficient than AMS). In addition rosindone X fails to fulfill the square root relationship as shown in figure 2, where the charges under the square root are given in weight percentages.

At low charges (0.01-0.09%) rosindone X catalyzes the delignification (on a molar base) as efficiently as anthraquinone ($r_M \sim 1$). Due to scatter of the lignin-free yields, quantification of the carbohydrate stabilization (v_M) is unreliable. However, the high v_M-value for sulfo derivative IX and the raw data of the experiments with X itself indicate that carbohydrate stabilization of rosindone is comparable in order of magnitude with that of anthraquinone. The breakdown of the square root relationship is best explained by the very low solubility of rosindone. Once

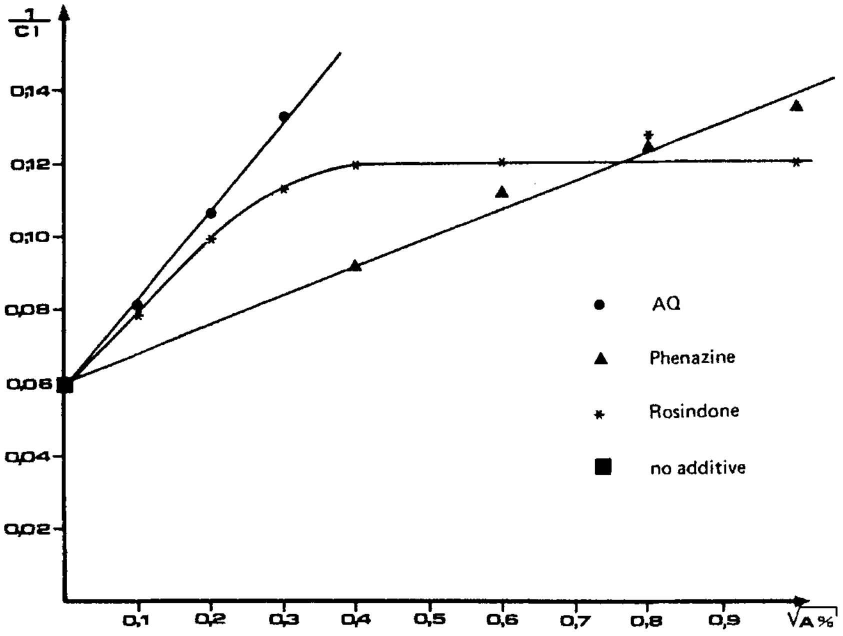


FIGURE 2: Square root relationship (see ref. 9)

the liquor is saturated with rosindone an increase of its charge does not increase the efficacy since undissolved rosindone cannot catalyze pulping. The influence of the solubility on the efficacy of a pulping additive is discussed in more detail in a separate paper[11].

CONCLUSIONS

It has been shown that the efficacies, based on weight percentages, of rosindone and its sulfonate as redox catalysts in alkaline pulping, are nearly as good as those of anthraquinone. Rosindone is the first pulping additive with a structural framework different from that of anthraquinone which is as efficient as anthraquinone using equimolar charges. From the scientific point of view this indicates that anthraquinone might not be the only valuable catalyst in the future. There still might be some possibilities for innovation. The present route of synthesis for rosindone is expensive compared to that of anthraquinone so that its commercial use is questionable.

EXPERIMENTAL

Carefully homogenized handmade chips of Scandinavian spruce (picea abies) were used. The pulping conditions were: Liquor to wood ratio 4:1, alkalinity 1.11 mol/l NaOH, time to 173°C 93 min., time at 173°C 120 min. Procedure and determination of efficacy parameters were the same as described earlier[9].

The non-commercial additives were synthesized according to routes described in the literature[16-22].

Polarographic measurements: Apparatus and solutions. DC polarograms were recorded with a Polarecord E 506 and a Metrohm E 608 programmer.

The phenazines, phenazones and rosindones were the same as those used in the pulping. The polarographic solutions were prepared by weighing equimolar amounts ($\sim 8.10^{-4}$m/l) of the respective additive in a polarographic cell, and adding 100 ml 1 N NaOH. After dissolution or homogenization of the additive by sonication (sonifier B 12, Branson Sonic Power Co, USA) for 2 min, 3.2 g spruce chips were transferred to the polarographic cell and treated for 2 further min by sonication.

All polarographic measurements were performed in deoxygenated solutions using a rotating, modified glassy carbon disc electrode (Metrohm E 628) as working electrode, a Pt wire as counter and a saturated calomel (SCE) electrode with a salt bridge as reference electrode.

After heating from 20 to 90°C in 30 min, DC polarograms were recorded periodically (every 6 min for the first, every 10 min for the second period). The surface of the working electrode was polished after each run. The half-wave potentials ($E_{1/2}$) given in tables 1-4 were measured after 90 min period at 90°C vs. SCE.

REFERENCES

1. B. Bach and G. Fiehn, Zellstoff Papier 21 (1): 3 (Jan. 1972)
2. H.H. Holton, Pulp Paper Can. 78 (10): T218 (1977)
3. H.H. Holton and F.L. Chapman, Tappi 60 (11): 121 (1977)
4. J.R. Obst, L.L. Landucci and N. Sanyer, Tappi 62 (1): 55 (1979)
5. R.C. Eckert, U.S. Pat. 4,134, 787 (Jan. 1979)
6. B.I. Fleming, G.J. Kubes, J.M. MacLeod and H.I. Bolker, Tappi 62 (6): 57 (1979)
7. R.C. Eckert and L. Amos, Tappi 63 (11): 89 (1980)
8. B.I. Fleming, J.M. MacLeod, G.J. Kubes and H.I. Bolker, Tappi 63 (12): 112 (1980)
9. D.P. Werthemann and O.J. Pekkala, Trans. Tech. Sect. CPPA 6 (3): 77 (Sept. 1980). Paper presented at the 1979 Canadian Wood Chemistry Symposium, at Harrison Hot Springs, B.C., Sept. 19-21,. 1979
10. D.P. Werthemann, Tappi 64 (3): 140 (1981)
11. D.P. Werthemann, Tappi: paper submitted
12. E. Heilbronner and H. Bock, Das HMO-Modell und seine Anwendung, Verlag Chemie, Weinheim/Bergst.: Vol. 1, p. 355 (1968)

13. J. Kelemen, Dyes and Pigments: 2, 73 (1981)

14. B.I. Fleming, G.J. Kubes, J.M. MacLeod and H.I. Bolker, Tappi 61 (6): 43 (1978)

15. W.H. Algar, A. Farrington, B. Jessup and P.F. Nelson, Appita 33 (1), 33 (1979)

16. F. Kehrmann and K.L. Stern, Ber. 41 (1908) 41

17. F. Kehrmann and E. Havas, Ber. 46 (1913) 341

18. F. Kehrmann, Ber. 56 (1923) 2385

19. F. Kehrmann, Ann. 290 (1896) 247

20. O. Fischer and E. Franck, Ber. 26 (1893) 179

21. Beilstein 25, 297-298

22. H. McIlwain, J. Chem. Soc. 1937, 1704

23. Scandinavian pulp, paper and bord testing comité: SCAN-C 29:72

24. B. Kyrklund and G. Strandell, Paperi ja Puu 51 (4a): 299-305 (1969)