Linear Free Energy Relationship in Naphthalene System. Kinetics of Oxidation of 4-Substituted 1-Naphthyl Methyl Sulphides with Peroxoanions

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The kinetics of the oxidation of several 4-substituted 1-naphthyl methyl sulphides and methyl 2-naphthyl sulphide with potassium peroxodisulphate and potassium peroxodiphosphate have been studied in 70% acetic acid–30% water (v/v) mixture. The results are in accord with rate-limiting electrophilic attack of the oxidants on the sulphide. The applicability of the Hammett equation to the rate data employing naphthalene and benzene substituent constants has been critically examined. Excellent results emerge in the correlation of rate constants with σ_p^+ constants in both oxidations. The diminution in the electron-withdrawing ability of the acetyl group present in the 4-position of the naphthyl ring has been attributed to the steric inhibition of resonance of the acetyl group by the proximate *peri*-hydrogen. The reactivity order of methyl phenyl, methyl 1-naphthyl, and methyl 2-naphthyl sulphides ($2\text{-}C_{10}H_7SMe > C_6H_5SMe > 1\text{-}C_{10}H_7SMe$) found in these oxidations has been explained on the basis of polar and steric effects.

Although the literature is replete with correlation studies of rate or equilibrium data of benzene derivatives,[1] relatively few such studies are found for naphthalene[2] derivatives. In naphthalene derivatives, there are many combinations between the positions of substituents and reaction centres. In the naphthalene system, the inductive and resonance contributions to substituent effects may differ from each other, depending upon the relative position of substituents in any single reaction.[3,4] Consequently, a study of the substituent effects on the naphthalene system will offer important information on the positional dependence of the transmittance of inductive and resonance effects in naphthalene derivatives. We report here the results of correlation studies on the oxidation of 4-substituted 1-naphthyl methyl sulphides by peroxoanions. It is pertinent to note that no correlation study has been reported hitherto on the reactivity data of methyl naphthyl sulphides.

Results and Discussion

Peroxodisulphate Oxidation.—The rate constants at different initial concentrations of methyl 1-naphthyl sulphide (MNS) and peroxodisulphate ion (PS) at constant ionic strength (maintained by the addition of $NaClO_4$) and $[H^+]$ are listed in Table 1. Plots of log [PS] against time afforded straight lines, from the slopes of which the pseudo-first-order rate constants (k_1) were evaluated. The first-order dependence of the reaction on [MNS] emerges from the gradient, 0.97 ± 0.04 (*r* 0.999, *s* 0.007) of the log–log plot of the rate constants and [MNS]. Further, a plot of k_1 *versus* [MNS] is linear showing that the reaction is second-order.

The data in Table 2 indicate that the rate is not significantly altered on increasing either $[H^+]$ or ionic strength. Addition of acrylamide to the reaction mixture in a nitrogen atmosphere failed to display polymerisation and hence a free-radical mechanism is ruled out. The rates of oxidation of all sulphides have been studied at 30, 40, and 50 °C. The data fit the Arrhenius equation and the activation parameters for the sulphides (Table 3) are in accordance with a rate-limiting S_N2-type mechanism.[5]

The foregoing observations support a mechanism involving an initial, rate-determining electrophilic attack of the oxidant on the sulphide resulting in a sulphonium ion intermediate followed by its fast conversion into sulphoxide as proposed for the PS oxidation of substituted phenyl alkyl sulphides.[6] This indicates that the structural variations in methyl phenyl and methyl naphthyl sulphides are not too large to cause differences in the mechanism.

Peroxodiphosphate Oxidation.—The rate constants at varying concentrations of methyl 1-naphthyl sulphide and peroxodiphosphate ion (PP) at constant ionic strength and $[H^+]$ are presented in Table 4. The plots of log [PP] *versus* time are linear indicating that the reaction is first order in the oxidant. The constancy of the second-order rate constants in Table 4 shows that the reaction is first order in the sulphide also.

Table 1. Pseudo-first-order (k_1) and second-order (k_2) rate constants for the oxidation of methyl 1-naphthyl sulphide with PS in 70% acetic acid–30% water (v/v) at 40 °C

$10^2[MNS]_0/M$	$10^3[PS]_0/M$	$10^5k_1{}^a/s^{-1}$	$10^3k_2{}^a/l\ mol^{-1}\ s^{-1}$
1.017	1.000	9.22 ± 0.16	9.07 ± 0.16
1.453	1.000	13.2 ± 0.39	9.08 ± 0.27
2.189	1.000	19.8 ± 0.24	9.05 ± 0.11
2.853	1.000	25.4 ± 0.46	8.90 ± 0.16
2.983	1.000	26.7 ± 0.84	8.95 ± 0.28
2.983	1.650	25.7 ± 0.95	8.62 ± 0.32
2.983	2.200	27.0 ± 0.48	9.05 ± 0.16
2.983	2.800	26.2 ± 0.42	8.78 ± 0.14

[a] The error quoted in *k* is the 95% confidence limit of the Student's *t* test.

Table 2. Influence of added perchloric acid and sodium perchlorate on the rate of oxidation of methyl 1-naphthyl sulphide with PS

$10^2[HClO_4]/M$	0.0000	1.014	4.056	6.084	8.112
$10^3k_2{}^a/l\ mol^{-1}\ s^{-1}$	4.33 ± 0.12	4.37 ± 0.20	4.77 ± 0.11	5.00 ± 0.04	5.20 ± 0.07
$10^2[NaClO_4]/M$	0.00	4.67	6.67	10.7	20.7
$10^3k_2{}^b/l\ mol^{-1}\ s^{-1}$	8.68 ± 0.14	8.82 ± 0.14	8.88 ± 0.11	9.08 ± 0.16	9.51 ± 0.76

[a] At [MNS] 1.915×10^{-2}M, [PS] 1.9×10^{-3}M, *T* 30 °C. [b] At [MNS] 1.984×10^{-2}M, [PS] 1.1×10^{-3}M, *T* 40 °C.

Table 3. Second-order rate constants and enthalpies and entropies of activation for the oxidation of 4-substituted 1-naphthyl methyl sulphides, methyl phenyl sulphide, and methyl 2-naphthyl sulphide by PS[a]

No.	Sulphide	10^3k_2/l mol^{-1} s^{-1}			$\Delta H^{\ddagger}$ [b]/kJ mol^{-1}	$-\Delta S^{\ddagger}$ [b] /J K^{-1} mol^{-1}
		30 °C	40 °C	50 °C		
1	Methyl phenyl	6.29 ± 0.11	11.9 ± 0.14	25.3 ± 0.43	54.0 ± 1.3	109 ± 4.3
2	Methyl 2-naphthyl	8.43 ± 0.31	16.5 ± 0.40	33.1 ± 1.2	53.1 ± 2.6	110 ± 8.9
	4-X-1-naphthyl methyl sulphides X =					
3	H	4.26 ± 0.31	8.93 ± 0.20	19.1 ± 0.38	58.5 ± 3.1	97.8 ± 11
4	MeO	15.8 ± 0.53	30.0 ± 0.54	57.5 ± 0.87	50.0 ± 1.8	115 ± 6.2
5	Me	7.37 ± 0.45	14.2 ± 0.29	30.2 ± 0.43	54.8 ± 2.6	106 ± 8.8
6	Et	6.84 ± 0.14	14.5 ± 0.28	28.5 ± 1.1	55.5 ± 2.1	103 ± 7.2
7	F	5.02 ± 0.26	10.1 ± 0.25	21.5 ± 0.27	56.6 ± 2.4	103 ± 8.2
8	Cl	3.88 ± 0.08	8.05 ± 0.23	17.2 ± 0.57	58.0 ± 2.2	100 ± 7.6
9	Br	3.61 ± 0.08	7.40 ± 0.17	15.3 ± 1.2	56.2 ± 3.4	107 ± 11
10	$COCH_3$	1.73 ± 0.12	4.16 ± 0.09	8.66 ± 0.01	63.0 ± 2.5	90 ± 8.5

[a] General conditions: [Sulphide] $\gg$ [PS] in 70% acetic acid–30% water (v/v) at I 0.02M. [b] The precision of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values was calculated by the method of Petersen *et al.*[37]

Table 4. Pseudo-first-order and second-order rate constants for the oxidation of methyl 1-naphthyl sulphide with PP in 70% acid–30% water (v/v) at 40 °C[a]

10^2[MNS]$_0$/M	10^3[PP]$_0$/M	10^5k_1/s^{-1}	10^3k_2/l mol^{-1} s^{-1}
1.015	1.000	11.9 ± 0.37	11.7 ± 0.36
1.522	1.000	17.7 ± 0.47	11.6 ± 0.31
2.029	1.000	23.7 ± 0.89	11.7 ± 0.44
3.044	1.000	35.9 ± 0.61	11.8 ± 0.20
2.537	1.000	29.2 ± 1.1	11.5 ± 0.43
2.537	1.500	28.4 ± 0.56	11.2 ± 0.22
2.537	2.000	28.7 ± 1.0	11.3 ± 0.39
2.537	2.500	29.7 ± 0.58	11.7 ± 0.23

[a] I 0.2M, [H$^+$] 0.0143M.

The data in Table 5 show that the reaction is acid-catalysed. The plot of log k_2 *versus* log [H$^+$] affords a straight line passing through the origin with a slope of 1.01 ± 0.28 (r 0.990, s 0.04). This shows that the reaction is first order in [H$^+$] and the active species[7a] is $H_3P_2O_8^-$. The reaction displays a negative salt effect (Table 5). Addition of acrylamide, the free-radical inhibitor, had no effect on the rate. The negative entropy of activation (Table 6) indicates an ordered transition state.[5] Similar observations have been reported for the oxidation of methyl phenyl sulphide (MPS) by PP.[7a] The active species $H_3P_2O_8^-$ attacks the sulphide in a slow step forming a sulphonium ion and a mechanism analogous to the one proposed for the oxidation of MPS by PP[7a] also operates here.

Table 5. Effect of perchloric acid and sodium perchlorate on the rate of oxidation of methyl 1-naphthyl sulphide with PP

10^2[$HClO_4$]/M	1.43	2.43	3.74	4.44	5.45
10^3k_2[a]/l mol^{-1} s^{-1}	4.69 ± 0.18	7.16 ± 0.40	12.8 ± 0.38	15.8 ± 0.78	18.4 ± 1.2
10^2[$NaClO_4$]/M	0.000	1.881	3.762	7.524	18.80
10^2k_2[b]/l mol^{-1} s^{-1}	3.34 ± 0.05	2.36 ± 0.07	1.98 ± 0.07	1.45 ± 0.05	1.17 ± 0.04

[a] At [MNS] 1.915 × 10^{-2}M, [PP] 1.0 × 10^{-3}M, T 30 °C. [b] At [MNS] 1.015 × 10^{-2}M, [PP] 1.0 × 10^{-3}M, T 40 °C.

Table 6. Second-order rate constants and enthalpies and entropies of activation for the oxidation of 4-substituted 1-naphthyl methyl sulphides, methyl phenyl sulphide, and methyl 2-naphthyl sulphide by PP[a]

No.	Sulphide	10^3k_2/l mol^{-1} s^{-1}			$\Delta H^{\ddagger}$ [b]/kJ mol^{-1}	$-\Delta S^{\ddagger}$ [b]/J K^{-1} mol^{-1}
		30 °C	40 °C	50 °C		
1	Methyl phenyl	7.33 ± 0.12	17.8 ± 0.30	43.2 ± 1.5	69.6 ± 1.8	56.6 ± 6.2
2	Methyl 2-naphthyl	10.5 ± 0.28	23.4 ± 0.78	52.0 ± 1.0	62.5 ± 2.1	76.9 ± 7.3
	4-X-1-naphthyl methyl sulphides X =					
3	H	4.90 ± 0.13	11.6 ± 0.32	29.0 ± 0.80	69.8 ± 2.2	59.4 ± 7.5
4	MeO	14.9 ± 0.55	35.5 ± 0.82	72.5 ± 3.0	61.9 ± 2.7	75.9 ± 9.3
5	Me	7.33 ± 0.37	19.1 ± 0.08	46.6 ± 2.3	72.7 ± 2.7	46.1 ± 9.2
6	Et	7.66 ± 0.18	17.9 ± 0.44	43.5 ± 1.6	68.1 ± 2.3	61.2 ± 7.8
7	F	5.43 ± 0.20	14.3 ± 1.3	29.5 ± 1.3	66.4 ± 4.7	69.2 ± 16
8	Cl	3.95 ± 0.15	10.8 ± 0.24	24.6 ± 1.1	71.9 ± 2.8	53.7 ± 9.5
9	Br	3.64 ± 0.08	9.17 ± 0.53	21.9 ± 0.60	70.5 ± 2.9	59.4 ± 9.9
10	$COCH_3$	2.19 ± 0.11	5.12 ± 0.10	12.7 ± 0.48	68.9 ± 2.9	68.8 ± 9.9

[a] General conditions: [Sulphide] $\gg$ [PP] in 70% acetic acid—30% water (v/v) at I 0.20M.

Table 7. Results of correlations of the rate data at 40 °C with substituent constants of naphthalene and benzene systems in PS and PP oxidations

No.	Substituent constant	ρ	r	s	Number of data points
		PS oxidation			
1	σ_{41}(FM)	-0.80 ± 0.20	0.970	0.07	8
2	σ_{41}(expl)	-0.95 ± 0.54	0.924	0.10	6[a]
3	σ_{41}^{+}	-0.51 ± 0.06	0.996	0.02	6[a]
4	ρ_p	-0.93 ± 0.33	0.942	0.09	8
5	$\sigma_p^{+}/\sigma_p^{-}$	-0.54 ± 0.10	0.984	0.05	8
6	σ_p^{+}	-0.66 ± 0.01	0.999	0.01	8[b]
		PP oxidation			
7	σ_{41}(FM)	-0.80 ± 0.16	0.980	0.05	8
8	σ_{41}(expl)	-0.90 ± 0.51	0.927	0.09	6[a]
9	σ_{41}^{+}	-0.47 ± 0.09	0.991	0.03	6[a]
10	σ_p	-0.96 ± 0.34	0.956	0.09	8
11	$\sigma_p^{+}/\sigma_p^{-}$	-0.53 ± 0.08	0.990	0.04	8
12	σ_p^{+}	-0.65 ± 0.07	0.994	0.03	8[b]

[a] The data points of ethyl and acetyl group are not included because of the nonavailability of constants. [b] For the acetyl group σ has been employed.

Correlation Analysis in PS and PP Oxidations of 4-*Substituted* 1-*Naphthyl Methyl Sulphides*.—The data in Tables 3 and 6 show that electron-releasing substituents accelerate and electron-withdrawing substituents retard the rates of oxidation of the sulphides with both oxidants in conformity with the proposed mechanisms.

With a view to studying the applicability of the Hammett relationship to these rate data (Tables 3 and 6) correlations have been performed using naphthalene [σ_{41}(FM),[8] σ_{41}(expl),[9] and σ_{41}^{+}[10]] and benzene (σ_p, σ_p^{+}, and σ_p^{-})[11] substituent constants. The results presented in Table 7 show that correlations with σ_{41}(FM), σ_{41}(expl), and σ_p constants are poor. The good correlations obtained with σ_{41}^{+} and σ_p^{+} indicate that the resonance effect dominates the inductive effect in these oxidations. This is due to the conjugation between the sulphide sulphur and the 4-substituent.

The good correlations of log k_2 with σ_{41}^{+} and σ_p^{+} suggest that either of these constants can be used for methyl naphthyl sulphides. This brings out the similarity of 4,1-naphthalene and 4,1-benzene systems in the transmission of substituent effects which is also justified by the existence of a linear relationship between the σ_{41}^{+} and σ_p^{+} constants (r 0.993, s 0.05, n 6). The σ_p^{+} constants are also found to correlate the rate data obtained in the oxidation of 6-substituted 2-naphthyl methyl sulphides.[12] Similar correlations with benzene substituent constants have been noted in ^{1}H and ^{13}C n.m.r. chemical shift data of 4,1- and 6,2-substituted naphthyl methyl sulphides.[13]

Because of the ability of sulphur to donate or accept electron density by the resonance effect, the rate data of substituted phenyl methyl sulphides have been successfully correlated with $\sigma_p^{+}/\sigma_p^{-}$ in many studies.[6,7,14] On the other hand, the 4-acetyl group in the naphthalene system is well behaved when its σ constant is used rather than σ^{-}, as indicated by a better correlation of the rate data with σ_p^{+} than with $\sigma_p^{+}/\sigma_p^{-}$ (Table 7). This suggests decreased electron-withdrawing ability for the acetyl group present in the 4-position of the naphthyl ring. This may presumably be ascribed to steric inhibition of resonance of the acetyl group caused by the proximate *peri*-hydrogen.

The negative sign of the ρ values is in conformity with the well documented nucleophilic behaviour of sulphides in general.[6,7,14] The smallness of the ρ values (ρ_{PS} -0.66 and ρ_{PP} -0.65 at 40 °C in log k_2 *versus* σ_p^{+}) leads to the inference that a relatively 'early' (reactant-like) transition state is involved in the rate-determining step. The ρ values (ρ_{PS} and ρ_{PP}) are nearly equal. This is not surprising as the two oxidants are isoelectronic and isostructural with almost equal oxidation potentials.[15]

Isokinetic Relationships.—As the plots of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the oxidations resulted in poor correlations, isokinetic temperatures have been calculated from the log–log plot[16] of rate constants at temperatures 30 and 50 °C. The values of β obtained in PS and PP oxidation are -764 K (r 0.999, s 0.01) and -455 K (r 0.991, s 0.12), respectively. The good correlations obtained in the relationship lead to the conclusion that there is no variation in the mechanism of oxidation[17] as the substituents are changed in both oxidations.

The Relative Reactivities of Methyl Phenyl, Methyl 1-*Naphthyl, and Methyl* 2-*Naphthyl Sulphides*.—The data in Tables 3 and 6 show the following order of reactivity in both oxidations: 2-$C_{10}H_7SMe$ > C_6H_5SMe > 1-$C_{10}H_7SMe$.

Because of the difference in the polarisabilities[18] of the 1- and 2-position of the naphthalene ring, 1-$C_{10}H_7SMe$ is anticipated to react at a faster rate than the 2-isomer. The lower rate of oxidation of the 1-$C_{10}H_7SMe$ than its 2-isomer could conceivably be caused by either steric strain or steric inhibition to solvation in the transition state due to the *peri*-hydrogen (8-H) of 1-$C_{10}H_7SMe$. These possibilities can be distinguished by the effect on $\Delta S^{\ddagger}$ since steric inhibition to solvation should increase while steric strain should decrease $\Delta S^{\ddagger}$.[19] The $\Delta S^{\ddagger}$ values (Tables 3 and 6) show the same trend with a higher value of $\Delta S^{\ddagger}$ for the 1-isomer favouring steric inhibition to solvation.

The higher rate of oxidation of methyl 2-naphthyl sulphide than methyl phenyl sulphide may be ascribed to the greater ability of the naphthyl system to accommodate the electron deficiency of the rate-determining transition state. This observation is in agreement with the σ^{+} value (-0.132)[20] of the 3,4-benzo substituent.

Experimental

M.p.s and b.p.s are uncorrected. The ^{1}H n.m.r. spectra have been recorded on a Varian EM-360L 60 MHz n.m.r. spectrometer using tetramethylsilane as an internal standard.

The oxidants potassium peroxodisulphate (G. R. E. Merck) and tetrapotassium peroxodiphosphate (FMC Corporation) were used after crystallisations from water and methanol–water, respectively. Acetic acid was purified by a standard procedure.[21] Methyl phenyl sulphide was obtained by methylation of benzenethiol followed by distillation, b.p. 189—190 °C (lit.,[22] 187—188 °C). Methyl 1-naphthyl sulphide, b.p. 141—143 °C at 5 mmHg (lit.,[23] 120—145 °C at 1 mmHg), and its 2-isomer, m.p. 60 °C (lit.,[24] 61—62 °C), were prepared from their corresponding thiols.[25,26]

Friedel–Crafts acetylation of methyl 1-naphthyl sulphide employing the method of Burton and Hu[27] yielded 4-methylthio-1-acetonaphthone, m.p. 74—75 °C (from EtOH); δ ($CDCl_3$) 2.60 (3 H, s), 2.70 (3 H, s), 7.28 (1 H, d, J 8 Hz), 7.55—7.72 (2 H, m), 7.92 (1 H, d, J 8 Hz), 8.31 (1 H, m), and 9.02 (1 H, m). Wolff–Kishner reduction[28] of the foregoing sulphide afforded 4-ethyl-1-naphthyl methyl sulphide, b.p. 171—173 °C at 10 mmHg; δ($CDCl_3$) 1.22 (3 H, t, J 7.7 Hz), 2.30 (3 H, s), 2.88 (2 H, q, J 7.7 Hz), 7.00—7.67 (4 H, m), 7.83—8.13 (1 H, m), and 8.37—8.67 (1 H, m). 4-Methoxy-1-naphthyl methyl sulphide, m.p. 65—66 °C (from EtOH); δ($CDCl_3$) 2.46 (3 H, s), 3.97 (3 H, s), 6.75 (1 H, d, J 7.8 Hz), 7.37—7.87 (3 H, m), and 8.20—8.60 (2 H, m) was obtained from 4-methoxynaphthalene-1-thiol.[29] 4-Methyl-1-naphthyl methyl sulphide, b.p. 160—161 °C at 13 mmHg; δ($CDCl_3$) 2.38 (6 H, s), 6.87—7.67 (4 H, m), 7.67—7.97 (1

H, m), and 8.33—8.63 (1 H, m), 4-chloro-1-naphthyl methyl sulphide, b.p. 187—189 °C at 11 mmHg; δ($CDCl_3$) 2.25 (3 H, s), 6.95 (1 H, d, *J* 8 Hz), 7.13—7.67 (3 H, m), and 8.13—8.43 (2 H, m), and 4-bromo-1-naphthyl methyl sulphide, b.p. 213—215 °C at 14 mmHg (lit.,[30] 157—158 °C at 0.2 mmHg); δ($CDCl_3$) 2.20 (3 H, s), 6.80 (1 H, d, *J* 8 Hz), 7.10—7.70 (3 H, m), and 8.00—8.39 (2 H, m), were obtained from their corresponding sulphonyl chlorides.[31,32] 4-Fluoronaphthalene-1-sulphonyl chloride, m.p. 80 °C, obtained from 1-fluoronaphthalene by employing the method of Huntress and Carten,[32] upon reduction and methylation yielded 4-fluoro-1-naphthyl methyl sulphide, b.p. 160—162 °C at 14 mmHg (lit.,[33] 100—102 °C at 1 mmHg); δ($CDCl_3$) 2.28 (3 H, s), 6.73—7.63 (4 H, m), and 7.93—8.50 (2 H, m). The purity of the sulphides was checked with t.l.c. and ^{1}H and ^{13}C n.m.r. spectroscopy. The 4-methoxy-, 4-ethyl-, and 4-acetyl-1-naphthyl methyl sulphides gave satisfactory elemental analyses.

Kinetic Procedure.—The rate measurements were performed under pseudo-first-order conditions in 70% acetic acid–30% water (v/v) at constant ionic strength and $[H^+]$ with a large excess of [sulphide] over the oxidants. The PS oxidation was followed by estimating the unreacted oxidant by the method of Kolthoff and Carr.[34] The PP oxidation was studied by the method of Gupta and his co-workers.[35] All the reactions were homogeneous. The kinetics were followed up to 60—70% of the reaction. The correlation coefficients of all first-order plots were at least 0.996. The pseudo-first-order rate constants (k_1) were evaluated by the least-squares method. The second-order rate constants were obtained by dividing the pseudo-first-order rate constants by [sulphide]. The accuracy of the *k* value is presented in terms of 95% confidence limits of the 'Student *t*'.[36] The least-squares and regression analyses were carried out by using a Micro 2200 computer (Hindustan Computers).

Stoicheiometry.—Solutions of methyl 1-naphthyl sulphide and excess of oxidant (PS or PP) were allowed to react overnight at 40 °C. Estimation of the unreacted oxidant showed that the stoicheiometry was 1 : 1 in both PS and PP oxidations.

Product Analysis.—After *ca.* 70% completion of the reaction of 1-$C_{10}H_7SMe$ with PS as well as PP in actual kinetic runs, the reaction mixture in each case was extracted with chloroform, dried, evaporated, and the resultant product analysed by t.l.c. Comparison of the R_F values of the product mixture with those of authentic samples of sulphoxide and sulphone showed that sulphoxide was the only product formed in this reaction.

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