Kinetics and Mechanism of the Pyridinolysis of Benzyl Bromides in Dimethyl Sulfoxide

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Nucleophilic substitution reaction of Y-benzyl bromide with X-pyridines are investigated in DMSO at 45.0 °C. Biphasic rate dependence is observed on varying the substituents in the substrate (Y) as well as in the nucleophile (X). The two well-defined straight lines in the Hammett (ρ_Y) and Brönsted (β_X) plots are interpreted to indicate the changes in transition-state structure, a decrease in bond cleavage as the substituent on the substrate is changed from electron-donors ($\sigma_Y < 0$) to electron-acceptors ($\sigma_Y > 0$), and an increase in the extent of bond formation with the corresponding changes of the substituent on the pyridine. A Jencks' type analysis of separate polar (ρ) and resonance (ρ^r) effects can also be accounted for by the change of the transition-state structure, not by the variable combination of polar and resonance effects.

Introduction

Nucleophilic substitution reactions of benzyl halides have been shown to proceed through an unimolecular, bimolecular or mixed substitution mechanism depending on the substrate, nucleophile and solvent polarity.[1,2f] In almost all Hammett correlations of the reactions of benzyl halides, however, U-shaped curves with a minimum at the unsubstituted compound, or biphasic dependence of the rate with a break at the unsubstituted compound are observed, when substituent, σ_Y, on the benzene ring is varied.[2] For this behavior, three explanations are advanced[3] : (i) Change of mechanism from S_N2 to S_N1 on going from electron-withdrawing to electron-donating substituents. (ii) Change in the transition state (TS) structure for a single mechanism with a differing balance of bond formation and cleavage. (iii) Differing balance of polar and resonance effects by different substituents to stabilize the TS. A variable combination of polar and resonance effects has been described by the use of a modified Yukawa-Tsuno equation,[3,4] eq. 1. This equation is based on the use of separate ρ and ρ^r parameters for polar

$$\log (k/k_o) = \rho\sigma + \rho^r (\sigma^+ - \sigma^-) \qquad (1)$$

and resonance effects, respectively, as Taft and others[5] have proposed, with preserving the simplicity of the Yukawa-Tsuno approach.[4] In this work, we carried out kinetic studies of the reaction of Y-benzyl bromides with X-pyridines in dimethyl sulfoxide (DMSO) at 45.0 °C. We varied both substituents X and Y on the nucleophile and substrate, respectively, eq. 2, to represent relatively wide range of electron-

$$XC_6H_4N + YC_6H_4CH_2Br \xrightarrow[\text{45.0 °C}]{\text{DMSO}} XC_6H_4\overset{+}{N}CH_2C_6H_4Y + Br^- \qquad (2)$$
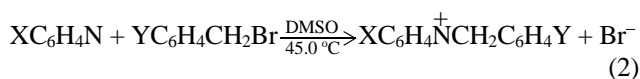
X = *p*-CH$_3$O, *p*-CH$_3$, *p*-C$_6$H$_5$CH$_2$, H, *m*-C$_6$H$_5$, *m*-CH$_3$CO, *p*-CH$_3$CO, *p*-CN or *m*-CN

Y = *p*-CH$_3$, *m*-CH$_3$, H, *m*-Cl, *m*-CN, *p*-CN, *m*-NO$_2$ or *p*-NO$_2$

donating and electron-withdrawing substituent effects. The objective of this work is to present most plausible explanations for the biphasic rate dependence on the substituents in the nucleophile (X) as well as in the substrate (Y). We have determined the cross-interaction constants, ρ_{XY} in eqs. 3,[6] to assist our interpretation of the rate data.

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \qquad (3a)$$
$$\rho_{XY} = \partial\rho_Y / \partial\sigma_X = \partial\rho_X / \partial\sigma_Y \qquad (3b)$$

Results and Discussion

The pseudo-first-order rate constants observed (k_{obs}) for all the reaction obeyed eq. 4 with negligible $k_o(\cong 0)$ in dimethyl sulfoxide. The second-order rate constants, k_2 ($M^{-1}s^{-1}$) summerized in Table 1, were determined

$$k_{obs} = k_o + k_2[Py] \qquad (4)$$

merized in Table 1, were determined using eq. 4 with at least five pyridine concentrations, [Py]. No complications were found in the determination of k_{obs} and also in the linear plots of eq. 4, suggesting that there is no noticeable side reactions and the overall reaction follows the route given by eq. 2. The rate is faster with a stronger nucleophile ($\delta\sigma_X < 0$) and a stronger electron donor substituent in the substrate ($\delta\sigma_Y < 0$) as normally expected for a nucleophilic substitution reaction with a positive charge development on the reaction center, C_α, in the TS.

Comparison of rates for the reactions of benzyl bromide with pyridine in methanol ($k_2 = 55.5 \times 10^{-5}$ M^{-1} s^{-1} at 50.0 °C[7]: $\varepsilon = 32.7$), DMF ($k_2 = 394 \times 10^{-5}$ M^{-1} s^{-1} at 50.0 °C[7]: $\varepsilon = 37.0$) and DMSO ($k_2 = 894 \times 10^{-5}$ M^{-1} s^{-1} at 45.0 °C: $\varepsilon = 46.7$) shows that the rate is the greatest in DMSO: this is a reflection of the greatest dielectric constant (ε) rendering the greatest stability to the dipolar TS while these is no ground

Table 1. Rate constants, k_2 ($\times 10^3$ M^{-1} s^{-1}), for the reactions of Y-benzyl bromides with X-pyridines in dimethyl sulfoxide at 45.0 ℃

Y \ X	pK_a[d]	p-CH₃	m-CH₃	H	m-Cl	m-CN	p-CN	m-NO₂	p-NO₂	ρ_Y[f]	ρ_Y[g]
p-CH₃O	6.58	41.7	27.5	20.0	18.6	16.6	15.8	15.1	14.1	-1.87±0.05 (0.999)	-0.28±0.02 (0.992)
p-CH₃	6.03	31.6	19.5	13.5	12.6	11.7	11.0	10.2	9.55	-2.17±0.05 (0.999)	-0.29±0.05 (0.964)
p-C₆H₅CH₂	5.59	23.3	15.7	11.2	10.0	9.55	9.12	8.91	8.51	-1.86±0.11 (0.998)	-0.17±0.02 (0.978)
H	5.21	18.9	11.4	8.94	8.71	8.29	7.91	7.55	7.06	-1.93±0.01 (0.995)	-0.21±0.06 (0.952)
m-C₆H₅	4.87	15.8	10.6	6.76	6.46	6.17	5.89	5.25	4.90	-2.15±0.29 (0.991)	-0.28±0.08 (0.908)
m-CH₃CO	3.10	5.83	3.64	2.63	2.51	2.29	2.00	1.82	1.58	-2.03±0.01 (0.999)	-0.48±0.09 (0.952)
p-CH₃CO	2.30	3.09	1.78	1.12	0.741	0.661	0.589	0.525	0.501	-2.58±0.13 (0.999)	-0.43±0.06 (0.975)
p-CN	1.86	2.24	1.20	0.794	0.525	0.490	0.407	0.355	0.316	-2.65±0.04 (0.998)	-0.55±0.12 (0.939)
m-CN	1.35	1.20	0.671	0.389	0.251	0.210	0.195	0.191	0.182	-2.85±0.24 (0.997)	-0.34±0.02 (0.994)
ρ_X[a]		-1.32±0.05 (0.998)[e]	-1.33±0.06 (0.997)	-1.38±0.10 (0.991)	-1.33±0.13 (0.986)	-1.24±0.12 (0.986)	-1.23±0.13 (0.985)	-1.28±0.17 (0.974)	-1.28±0.18 (0.973)		
ρ_X[b]		-3.43	-4.15	-4.15	-5.00	-5.19	-5.06	-4.90	-4.69		
β_X[a]		0.25±0.01 (0.999)	0.25±0.02 (0.993)	0.26±0.02 (0.995)	0.25±0.02 (0.993)	0.24±0.01 (0.995)	0.23±0.02 (0.991)	0.24±0.03 (0.971)	0.23±0.04 (0.952)	ρ_{XY}[h] =-0.91	ρ_{XY}[i] =-0.29
β_X[c]		0.38±0.03 (0.993)	0.42±0.02 (0.998)	0.46±0.03 (0.996)	0.56±0.04 (0.995)	0.58±0.05 (0.993)	0.57±0.04 (0.996)	0.55±0.04 (0.994)	0.54±0.03 (0.997)		

[a]X = p-CH₃O, p-CH₃, p-C₆H₅CH₂, H, m-C₆H₅. [b]X = m-CH₃CO, m-CN. [c]X = m-CH₃CO, p-CH₃CO, p-CN, m-CN. [d] pK$_a$ values in water at 25 ℃; ref. 8a. [e]Correlation coefficient. [f]Y = p-CH₃, m-CH₃, H, The σ values were taken from Hansch, C.; Leo, A.; Taft, R. W., *Chem. Rev.*, **1991**, 91, 165. [g]Y = m-Cl, m-CN, m-NO₂, p-NO₂. (h) Y = p-CH₃, m-CH₃, H. Correlation coefficient was better then 0.977. [i]Y = m-Cl, m-CN, p-CN, m-NO₂, p-NO₂. Correlation coefficient was better then 0.969.

state stabilizing effect of hydrogen bonding (by a protic solvent such as MeOH).

The Hammett plots (Figure 1) for the substituent variation in the substrate show curvature with a break point at Y = H analogously to other nucleophilic reactions of substituted benzyl halides.[2f,g] The approximate slopes, ρ_Y, for the two linear parts are shown in Table 1. For the electron donors, $\sigma_Y < 0$, the slopes are large negative (ρ_Y = -1.9~-2.9), whereas for the electron acceptors, $\sigma_Y > 0$, the magnitude of ρ_Y values is much smaller (ρ_Y = -0.2~-0.6). The negative sign of ρ_Y indicates positive charge development on the benzylic carbon (C_α), and hence implies a greater extent of bond cleavage than bond formation in the TS. Thus resonance stabilization of positive charge on C_α by an electron-donor leads to a large extent of bond cleavage whereas an electron acceptor substituent destabilizes the cationic charge by polar effect leading to a lower extent of bond cleavage in the TS. On closer examination of the ρ_Y values, we note that the magnitude of ρ_Y, and hence the extent of bond cleavage, is somewhat smaller for the reactions with basic pyridines ($\sigma_X < 0$) than those with less basic pyridines ($\sigma_X > 0$). This suggests that the degree of bond making is smaller with the basic nucleophiles than with weakly basic nucleophiles (*vide infra*), which in turn leads to a lesser degree of bond cleavage with the basic pyridines, *i.e.*, on earlier TS along the
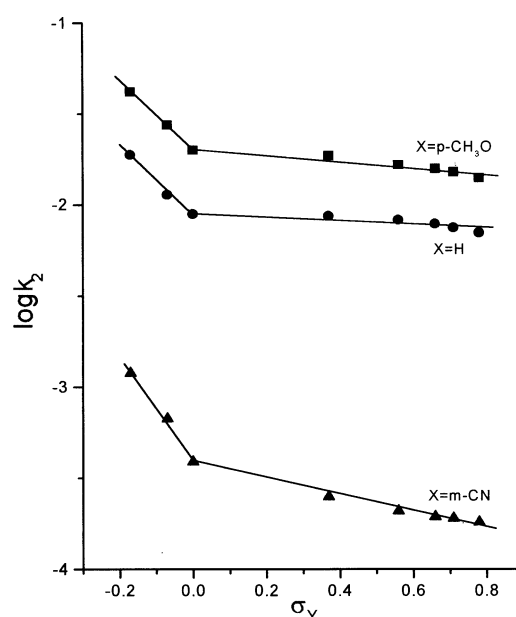
Figure 1. Hammett plots (ρ_Y) for the X-pyridinolysis of Y-benzyl bromides (for X=p-CH₃O, H and m-CN) in DMSO at 45.0 ℃.

reaction coordinate.

We have attempted a Jencks type analysis of the separate

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Table 2. Substituent effects for the attack of substituted pyridines (X) on substituted benzyl bromides

Substituted pyridine		$-\rho$	$-\rho^r$	$r^+ = \rho^r/\rho$
X	σ_X			
p-CH$_3$O	-0.27	0.2	1.7	8.5
p-CH$_3$	-0.17	0.2	1.8	9.0
p-CH$_2$C$_6$H$_5$	-0.09	0.2	1.6	8.0
p-CH$_3$CO	0.50	0.4	2.1	5.3
m-CN	0.56	0.4	2.3	5.8
p-CN	0.66	0.5	2.1	4.2

polar (ρ) and resonance effects (ρ^r)[3] according to eq. 1 in Table 2, where ρ is based on data for benzyl bromide and *p*-nitrobenzyl bromide and ρ^r is based on the deviation of the point for *p*-methylbenzyl bromide from the line defined by benzyl bromide and *p*-nitrobenzyl bromide.[3]

We note that for an electron donor substituent ($\sigma_X < 0$) in the nucleophile both the polar (ρ) and resonance effects (ρ^r) are smaller than those for an electron withdrawing X ($\sigma_X > 0$), but the overall resonance ratio ($r^+ = \rho^r/\rho$) is greater.[3,4] This simply shows that the degree of bond making is smaller but that of bond cleavage is quite large so that there is only small difference in the extent of bond cleavage depending on nucleophiles, X; as a result, the positive charge development which is facilitated by resonance effects of substituent Y becomes greater for an electron donor X than that for an electron acceptor X for which bond making is more advanced.

The Hammett plots for the variation of substituents in the nucleophile (X) also show curvatures with a break at X = *m*-CH$_3$CO ($\sigma_X = 0.38$), Figure 2. The negative slope of the electron-donor segment (including X = *m*-CH$_3$CO) is smaller ($\rho_X \simeq$ -1.3) than that of the electron-acceptor part ($\rho_X =$ -3.4~-5.2) which excludes *p*-CH$_3$CO and *p*-CN. These latter two acceptor substituents are known to have weak π-donor effect under the strong cationic charge of pyridinium ion (azonium ion, $\gtrdot \overset{+}{N}=$) and deviate positively from the logk$_2$ versus σ (*i.e.*, Hammett) plots. This is evident from the much enhanced rates for the two substituents in the plots, Figure 2. However these deviations from the Hammett plots disappear in the logk$_2$ versus pK$_a$ (*i.e.*, Brönsted) plots (Figure 3), since the basicity enhancing π-donor effect of the two acceptors is correctly reflected in the pK$_a$ measurement, in contrast to the lack of such π-donor effect (due to the lack of strong cationic functional center) in the determination of the σ constants. The Brönsted plots are also curved with a break at X = *m*-CH$_3$CO. The slope is greater for the weakly basic pyridines ($\beta_X = 0.4$~0.6) than for the basic nucleophiles ($\beta_X = 0.2$~0.3). These two well defined straight lines representing two different degrees of bond making by basic and weakly basic pyridines, respectively, provide evidence for a structural change of the TS, but not for a mechanistic change as we often found with acyl transfer reactions for which such biphasic dependence of the rates on the basicity of nucleophiles are normally taken as a mechanistic change from the
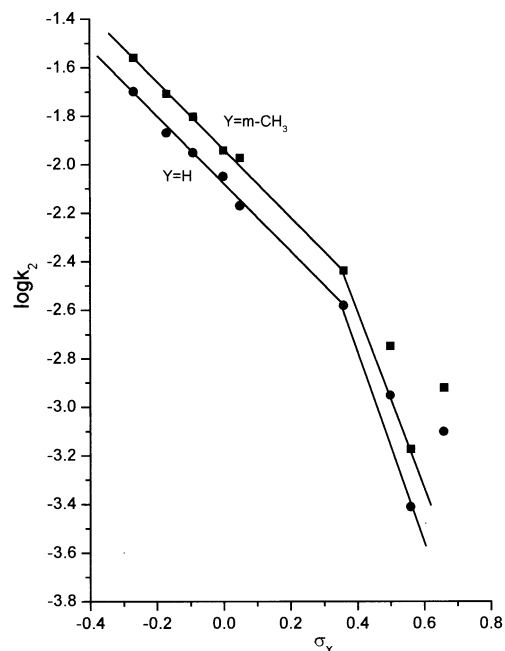
Figure 2. Hammett plots (ρ_X) for the X-pyridinolysis of Y-benzyl bromides (for Y = m-CH$_3$, H) in DMSO at 45.0 °C.
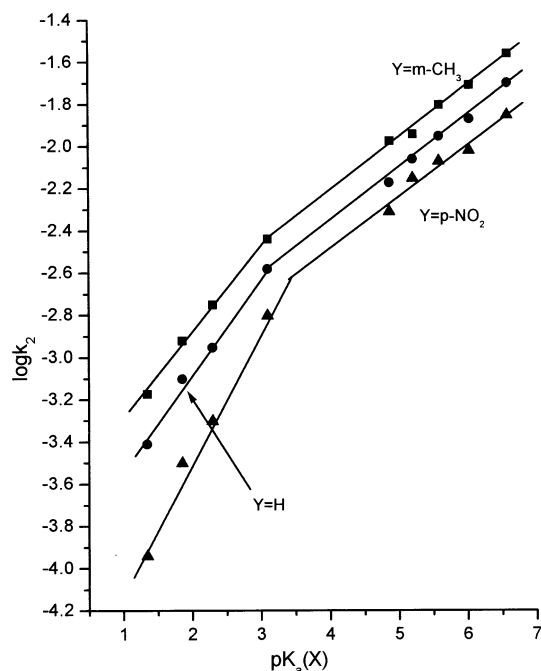
Figure 3. Hammett plots (β_X) for the X-pyridinolysis of Y-benzyl bromides (for Y = m-CH$_3$, H and p-NO$_2$) in DMSO at 45.0 °C.

rate-limiting breakdown to formation of a tetrahedral intermediate as the basicity of the amine nucleophile is increased.[9] In the present work, the existence of such an intermediate is out of question due to the strong nucleofugality of the bromide ion with the formation of a strong cationic reaction center.

This type of biphasic rate dependence on the nucleophile basicity is, however, rare, and in fact this is the first case we have encountered, in the S$_N$2 reactions. We can think of two

reasons for this behavior: (i) A relatively wide range of the pyridine pK_a values ($pK_a = 1.35 \sim 6.58$) used, and (ii) a strong interaction between the two reaction centers, the N atom on the pyridine and the benzylic carbon, C_α, in the TS which is well stabilized by a relatively strong dipolar aprotic solvent, DMSO.

The magnitudes of these β_X values suggest that bond formation is greater with weakly basic pyridines than with basic pyridines in agreement with our earlier prediction based on the magnitude of the ρ_Y values. The magnitudes of both ρ_X and β_X in Table 1 show very small variations depending on the substituents in the substrate Y. The magnitudes of ρ_X and β_X for the donor Y ($\rho_X = -3.4 \sim -3.7$, and $\beta_X = 0.4$) are slightly smaller than that for the acceptor Y ($\rho_X = -4.7 \sim -5.2$ and $\beta_X = 0.5 \sim 0.6$) with electron acceptor substituents in the nucleophile, X. For the electron donating substituents X in the nucleophile, there is very little variation in the magnitude of ρ_X and β_X depending on substituents Y.

The small variations of ρ_X and β_X depending on the substituents in the substrate (Y) indicate that the degree of bond formation is quite similar irrespective of the substituent Y. The large difference in the magnitude of ρ_Y between electron-donor Y ($-1.9 \sim -2.9$) and electron-acceptor Y ($-0.2 \sim -0.6$) is therefore largely attributable to the large difference in the positive charge developed in the TS, *i.e.*, in the extent of bond cleavage in the TS.

Since ρ_Y is dependent on σ_X, or alternatively ρ_X is dependent on σ_Y (Table 1), the reaction proceeds by a mechanism which is essentially S_N2 in all cases; thus there is no mechanistic change from S_N2 to S_N1, ruling out the explanation (i) above. The cross-interaction constants, ρ_{XY}, are -0.91 and -0.29 for the electron-donor and electron-acceptor Y, respectively. The former is a typical value obtained for S_N2 reactions of benzyl derivatives.[6] The latter value ($\rho_{XY} = -0.29$) is somewhat smaller, which is most probably due to the lower positive charge in C_α leading to a weaker electrostatic interaction between the two charged reaction centers on the pyridine nucleophile and substrate in the TS.[3] The fact that there are two distinct linear portions both for ρ_X (β_X) and ρ_Y supports the contention that there are changes in the TS structure (explanation ii) depending on the substituents. If there were a variable combination of polar and resonance effects (explanation iii) the ρ^+ value in Table 2 should exhibit gradual continuous change,[3] not discontinuously in roughly two parts as obtained in Table 2.

The activation parameters (Table 3) are within the range of values normally observed for S_N2 reactions of benzyl derivatives.[7]

In summary, the pyridinolysis of benzyl bromides in DMSO proceeds by the S_N2 mechanism. There are structural changes of the TS as the substituent in the substrate is changed, and also as the substituent in the nucleophile is changed, as evidenced by the biphasic dependences of rates on the structural parameters, σ_Y and $pK_a(X)$, respectively.

Experimental Section

Materials. International Specialty Chemicals ACS grade dimethyl sulfoxide (DMSO) was used after two distillations. The pyridine nucleophiles, Aldrich GR, were used without further purification. Aldrich benzyl bromide substrates were used, which were redistilled or recrystallized before use.

Rate constant. Rates were measured conductimetrically at 45.0 ± 0.05 ºC. The conductivity bridge used in this work was a self-made computer automatic A/D converter conductivity bridge. Psudo-first-order rate constants, k_{obs}, were determined by the curve fitting analysis of the diskette data with a modified version of the Origin program, which fits conductance *vs* time data to the equation $A = A_\infty + (A_0 - A_\infty)\exp(-k_{obs} t)$, where A_∞, $A_0 - A_\infty$, and k_{obs} are iteratively optimized to achieve the best possible least-squares fit with a large excess of pyridine (Py); [benzyl bromide] $\simeq 1 \times 10^{-3}$ M and [Py] $= 0.03 \sim 0.24$ M. Second-order rate constants, k_2, were obtained from the slope of a plot of k_{obs} *vs* [Py] with more than five concentrations of pyridine, eq. 4. The k_2 values in Table 1 are the averages of more than three runs and were reproducible to within $\pm 3\%$.

Product analysis. *p*-Methylbenzyl bromide ($CH_3C_6H_4$-CH_2Br) was reacted with an excess of pyridine (C_5H_5N) with stirring for more than 15 half-lives at 45.0 ºC in dimethyl sulfoxide, and the products were isolate by evaporating the solvent under reduced pressure. The product mixture was treated with column chromatography (silica gel, 15% ethyl acetate / n-hexane). The same method was used for the reaction of p-methylbenzyl bromide ($BrCH_2C_6H_4CH_3$) with *m*-cyanopyridine (m-CNC_5H_4N). The product analysis data are given below.

$C_5H_5N^+$-$CH_2C_6H_4CH_3$. M.p. 86~87 ºC. δ_H, NMR (250 MHz, $CDCl_3$), 2.15 (3H, s, CH_3), 6.21 (2H, s, CH_2), 7.1-7.5 (4H, m, benzene), 8.4-9.6 (5H, m, pyridine), Mass, m/z 184 (M^+). (Calc. For $C_{13}H_{14}N$ (C, 84.8; H, 7.6. Found: C, 84.6; H, 7.7%)).

m-$CNC_5H_4N^+$-$CH_2C_6H_4CH_3$. M.p. 92-94 ºC. δ_H, NMR (250 MHz, $CDCl_3$), 2.15 (3H, s, CH_3), 6.23 (2H, s, CH_2), 7.1-7.4 (4H, m, benzene), 8.4-9.6 (4H, m, pyridine), Mass, m/z 209 (M^+). (Calc. For $C_{14}H_{13}N$ (C, 80.4; H, 5.7. Found :

Table 3. Activation parameters[a] for the reactions of Y-benzyl bromides with X-pyridines in dimethylsulfoxide

X	Y	T/ºC	k_2 ($\times 10^3$ M^{-1} s^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$-\Delta S^{\neq}$ (cal mol^{-1} K^{-1})
H	*p*-CH₃	35	9.17	14.0±0.6	23±1
		45	18.9		
		55	38.9		
H	*p*-NO₂	35	3.75	13.7±0.4	23±1
		45	7.06		
		55	16.8		
m-CN	*p*-CH₃	35	0.620	12.7±0.7	32±1
		45	1.20		
		55	2.32		
m-CN	*p*-NO₂	35	0.120	7.8±0.2	51±2
		45	0.182		
		55	0.277		

[a]Calculated by the Eying equation. Errors shown are standard deviations.

C, 80.5; H, 5.6%)).

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