

# Kinetics & Mechanism of Oxidation of Thiocyanate Ion by Chloramine-B & Bromamine-B in Alkaline Medium

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Kinetics and mechanism of oxidation of thiocyanate ion ( $\text{NCS}^-$ ) by chloramine-B (CAB) and bromamine-B (BAB) have been studied in the alkaline medium over a wide range of  $[\text{NCS}^-]$  and  $[\text{OH}^-]$ . The order in  $[\text{CAB}]$  is unity over the entire range of  $[\text{NCS}^-]$  (0.01-0.5 mol dm<sup>-3</sup>), fractional in  $[\text{NCS}^-]$  and inverse fractional in  $[\text{OH}^-]$ . The order in  $[\text{BAB}]$  is unity, zero in  $[\text{NCS}^-]$  and fractional in  $[\text{OH}^-]$ . Effects of added reaction products and variations in ionic strength and dielectric constant of the reaction medium on the rate have also been investigated. Mechanisms in conformity with the observed kinetics have been proposed and the corresponding rate laws deduced. The activation parameters have been computed from the rate constants of the rate-determining steps.

The kinetics of oxidation of  $\text{NCS}^-$  by hydrogen peroxide<sup>1</sup>, aqueous iodine<sup>2</sup>, Cr(VI) and V(V)<sup>3</sup>, Bi(V)<sup>4</sup> and chloramine-T<sup>5,6</sup> are reported in literature. As a part of our kinetic investigations employing N-halogeno-N-metallo reagents as oxidants<sup>7-9</sup> we report herein the results of investigations on the oxidation of thiocyanate ion by chloramine-B and bromamine-B in alkaline medium.

## Materials and Methods

Chloramine-B (CAB, sodium N-chlorobenzenesulphonamide) and bromamine-B (BAB, sodium N-bromobenzenesulphonamide) were prepared in the laboratory and then the purity was checked by (i) iodometric estimation of active halogen present in them and (ii) their infrared and fourier transform <sup>1</sup>H and <sup>13</sup>C NMR spectra. Aqueous stock solutions of the oxidants (0.1 mol dm<sup>-3</sup>) were prepared, standardised and stored in dark coloured bottles. Potassium thiocyanate (Merck, AR) was dried at 150°C and its purity checked by argentometric method<sup>10</sup>. All other reagents employed were of accepted grades of purity. The ionic strength of the medium was maintained at 0.5 mol dm<sup>-3</sup> by adding concentrated solution of sodium perchlorate.

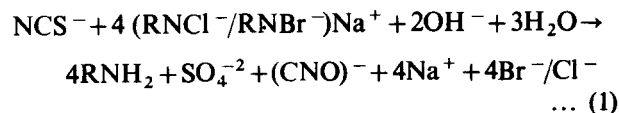
## Kinetic Measurements

The kinetic runs were made under pseudo-first order conditions with  $[\text{NCS}^-] \gg [\text{CAB}]_0$  or  $[\text{BAB}]_0$  (5 to 50 fold excess). The reactions were initiated by the rapid addition of measured quantities of CAB or BAB solution, thermally equilibrated at a desired temperature, to a mixture containing known amounts

of thiocyanate solution, sodium hydroxide, sodium perchlorate and water in glass stoppered pyrex boiling tubes, pre-equilibrated at the same temperature. The progress of the reaction was monitored for at least two half-lives by iodometric determination of unreacted oxidant in the reaction mixture at regular time intervals. The pseudo-first order rate constants were computed by the method of least squares and were reproducible within  $\pm 4\%$ .

## Stoichiometry and product analysis

The stoichiometries of CAB and BAB reactions with  $\text{NCS}^-$  were determined at different  $[\text{OH}^-]$  (0.01 to 0.1 mol dm<sup>-3</sup>) by thermally equilibrating solutions containing  $\text{NCS}^-$  and oxidant in different ratios at 303 K for 24 hr. The cyanate and sulphate ions among the reaction products were detected by standard tests<sup>11</sup>. Benzenesulphonamide (BSA), the reduced product of the oxidants was detected by TLC using ether-chloroform-*n*-butanol (2:2:1, v/v) as the solvent with iodine as the detecting reagent ( $R_F = 0.88$ ). Further the sulphate was quantitatively estimated by standard methods<sup>10</sup>. The stoichiometry observed may be represented by Eq. (1).



where  $\text{R} = \text{C}_6\text{H}_5\text{SO}_2$ .

## Results

Kinetics of reactions were studied over a wide range of  $[\text{NCS}^-]$  (0.002-2.0 mol dm<sup>-3</sup>) at different  $[\text{OH}^-]$  (Tables 1-3) and the orders in  $[\text{NCS}^-]$  and  $[\text{OH}^-]$  were determined from the log-log plots of  $k_{\text{obs}}$  and  $[\text{NCS}^-]$  or  $[\text{OH}^-]$ .

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Table 1—Effect of Varying [Reactants] on Rate of Oxidation of  $\text{NCS}^-$  by Chloramine-B in Alkaline Medium (figures in parentheses are the measured pH values)

$10^3[\text{CAB}]$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}^a$ (s <sup>-1</sup> ) at $[\text{NCS}^-]$ (mol dm <sup>-3</sup> )			$10[\text{NCS}^-]$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}^b$ (s <sup>-1</sup> ) at $[\text{OH}^-]$ (mol dm <sup>-3</sup> )			
	0.01 <sup>a1</sup>	0.1 <sup>a2</sup>	0.5 <sup>a3</sup>		0.01 <sup>b1</sup>	0.1 <sup>b2</sup>	$10[\text{NCS}^-]$ (mol dm <sup>-3</sup> )	0.025 <sup>b3</sup>
0.2	1.59	2.97(12.89)	—	0.02	0.38	—	2.5	7.8(12.2)
0.5	1.59	2.97(12.89)	—	0.05	0.76	—	5.0	10.2(12.3)
1.0	1.54	2.97(12.90)	—	0.1	1.59	0.51(12.93)	10.0	13.8(12.3)
2.0	1.59	2.97(12.89)	9.8	0.2	2.50	0.76(12.92)	15.0	16.2(12.3)
5.0	—	2.97(12.90)	10.2	0.5	6.07	1.59(12.90)	20.0	20.0(12.3)
10.0	—	—	10.2	1.0	9.97	2.97(12.91)	—	—
20.0	—	—	10.2	2.0	—	5.30(12.91)	—	—
				4.0	—	10.5(12.91)	—	—

<sup>a</sup>  $10^2[\text{OH}^-]$  (mol dm<sup>-3</sup>) = 1.0 (1), 10.0 (2), 2.5 (3); temp (K) = 313 (1 & 2), 303 (3).

<sup>b</sup>  $10^3[\text{CAB}]$  (mol dm<sup>-3</sup>) = 0.5 (1), 1.0 (2 & 3); temp (K) = 313 (1 & 2), 303 (3).

 Table 2—Effect of Varying  $[\text{OH}^-]$  on Rate of Oxidation of Thiocyanate Ion by Chloramine-B

$10^2[\text{OH}^-]$ (mol dm <sup>-3</sup> )	$10^3[\text{CAB}]$ (mol dm <sup>-3</sup> )	$10[\text{NCS}^-]$ (mol dm <sup>-3</sup> )	pH	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
0.1	0.5	0.1	—	7.7
0.2	0.5	0.1	—	4.6
0.5	0.5	0.1	—	2.2
1.0	0.5	0.1	—	1.6
2.0	0.5	0.1	—	1.2
5.0	0.5	0.1	—	0.85
10.0	0.5	0.1	—	0.69
1.0	1.0	1.0	12.0	10.7
2.0	1.0	1.0	12.3	5.8
5.0	1.0	1.0	12.7	4.5
10.0	1.0	1.0	12.9	3.0
20.0	1.0	1.0	13.3	1.9
50.0	1.0	1.0	13.5	1.2
0.5	5.0	5.0	11.7	20.6
1.0	5.0	5.0	11.8	13.9
2.5	5.0	5.0	12.3	10.2
5.0	5.0	5.0	12.6	7.6

## (a) Oxidation by chloramine-B

The concentration of CAB was varied at three initial  $[\text{NCS}^-]$  (0.01, 0.1 and 0.5 mol dm<sup>-3</sup>). The plots of  $\log([\text{CAB}]_0/[\text{CAB}])$  versus time were linear at least upto 75% completion of the reaction in all the cases except at low  $[\text{NCS}^-]$  under the condition  $[\text{NCS}^-] \ll [\text{OH}^-]$ . The rates were unaffected by change in  $[\text{CAB}]$  except under the condition when  $[\text{NCS}^-] \ll [\text{OH}^-]$ , suggesting the order to be unity in  $[\text{CAB}]$  over the entire range of  $[\text{NCS}^-]$  (0.002-2.0 mol dm<sup>-3</sup>). The rate increased with increase in  $[\text{NCS}^-]$  (Table 1) with fractional order dependence. The magnitude of fractional order in  $[\text{NCS}^-]$  (Table 4) decreased further with increase in  $[\text{NCS}^-]$ . The rate decreased with increase in  $[\text{OH}^-]$  (0.001-0.5 mol dm<sup>-3</sup>) with fractional order in  $[\text{OH}^-]$  in all the cases. pH of the reaction mixtures were measured as  $[\text{CAB}]$ ,  $[\text{NCS}^-]$  and  $[\text{OH}^-]$  were varied (Tables 1 and 2). The pH of the reaction mixtures changed only when  $[\text{OH}^-]$  was

 Table 3—Effect of Varying [Reactant] and  $[\text{OH}^-]$  on Rate of Oxidation of  $\text{NCS}^-$  by Bromamine-B in Alkaline Medium at 303 K ( $\mu = 0.5$  mol dm<sup>-3</sup>)

$10^3[\text{BAB}]^a$ (mol dm <sup>-3</sup> )	pH <sup>b</sup>	$10^4 k_{\text{obs}}$ s <sup>-1</sup> at $[\text{NCS}^-]$ (mol dm <sup>-3</sup> )		$10[\text{NCS}^-]^c$ (mol dm <sup>-3</sup> )	pH <sup>b</sup>	$10^4 k_{\text{obs}}$ s <sup>-1</sup>	$10^2[\text{OH}^-]^d$ (mol dm <sup>-3</sup> )	pH <sup>b</sup>	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> ) at $[\text{NCS}^-]$ (mol dm <sup>-3</sup> )	
		0.05	0.1						0.05	0.1
0.5	12.61	12.8	12.7	0.25	12.63	12.7	0.5	11.43	2.0	2.1
1.0	12.60	12.8	12.7	0.50	12.64	12.8	1.0	—	4.0	4.0
2.0	12.59	12.7	12.7	1.0	12.63	12.7	2.5	12.38	—	8.1
5.0	12.64	12.8	12.7	2.0	12.63	12.7	5.0	12.64	12.7	12.7
10.0	12.55	12.8	12.7	4.0	12.61	12.7	10.0	12.89	26.5	25.8
20.0	12.58	12.8	12.7	5.0	12.60	12.7	15.0	13.05	—	34.9
							20.0	13.15	45.4	44.9

<sup>a</sup>  $10^2[\text{OH}^-] = 5.0$  mol dm<sup>-3</sup>.

<sup>b</sup> Measured pH values of the reaction mixture.

<sup>c</sup>  $10^2[\text{OH}^-] = 5.0$  mol dm<sup>-3</sup>;  $10^3[\text{BAB}] = 5.0$  mol dm<sup>-3</sup>.

<sup>d</sup>  $10^3[\text{BAB}] = 5.0$  mol dm<sup>-3</sup>.

Table 4—Observed Orders and Activation Parameters for the Oxidation of Thiocyanate Ion by Chloramine-B &amp; Bromamine-B

Order observed in	Around [NCS <sup>-</sup> ] (mol dm <sup>-3</sup> )			Around [NCS <sup>-</sup> ] (mol dm <sup>-3</sup> )	
	0.01	0.1	0.5	0.05	0.1
	CAB			BAB	
[OX]	1	1	1	1	1
[NCS <sup>-</sup> ]	0.87	0.87	0.43	0	0
[OH <sup>-</sup> ]	-0.52	-0.56	-0.42	0.84	0.85
log A	26.4			7.4	
Ea (kJ mol <sup>-1</sup> )	172.3			56.5	
ΔH‡ (kJ mol <sup>-1</sup> )	169.7			54.0	
ΔS‡ (JK <sup>-1</sup> )	62.1			-24.9	
ΔG‡ (kJ mol <sup>-1</sup> )	150.3			61.5	

varied. The rates remained unaffected by the addition of the reaction products, BSA and Cl<sup>-</sup> at both low and high [NCS<sup>-</sup>]. Variations of ionic strength of the medium had little effect on the rate.

#### (b) Oxidation by bromamine-B

Although the kinetic order in [BAB] was dependent on [NCS<sup>-</sup>] no definite kinetics could be established at low [NCS<sup>-</sup>] (0.01 mol dm<sup>-3</sup>). At this concentration log ([BAB]<sub>0</sub>/[BAB]) versus time plots were linear but the rate varied with the change in [BAB].

At high [NCS<sup>-</sup>] (~0.03-0.5 mol dm<sup>-3</sup>) first order plots were linear at least upto 75% completion of the reaction. The pseudo-first order rate constants increased with increase in [OH<sup>-</sup>] (Table 3) indicating a fractional order of about 0.8 in [OH<sup>-</sup>]. But the rate was unaffected by the change in [NCS<sup>-</sup>] in the range of 0.025-0.5 mol dm<sup>-3</sup>. The rate increased slightly with increase in ionic strength of the medium. Rate constant at μ=0.105, 0.5 and 1.0 mol dm<sup>-3</sup> were 11.8, 12.7 and 13.2 × 10<sup>-4</sup>s<sup>-1</sup>, respectively. Addition of the reaction products, BSA and Br<sup>-</sup> had no effect on the rate.

#### Dependence of rate on dielectric constant

The rates increased with decrease in dielectric constant of the medium effected by changing the solvent composition by adding methanol. The true effect of the dielectric constant of the medium was determined by varying [NCS<sup>-</sup>] at different solvent compositions and constants of the rate limiting steps were calculated at each dielectric constant (Table 5) as described under discussion. The plots of logarithm of these constants versus 1/D plots were linear with positive slopes in both the cases.

The substrate concentration was also varied at different temperatures with both the oxidants and constants of the rate-limiting steps were calculated as functions of temperature. These constants were used to compute the activation parameters in both the cases (Table 4).

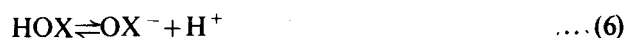
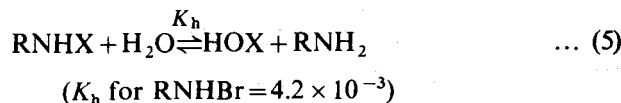
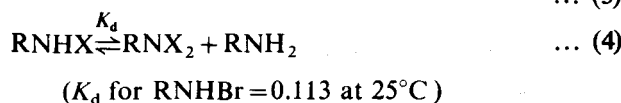
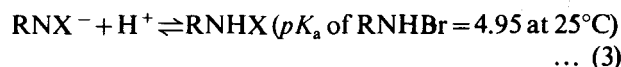
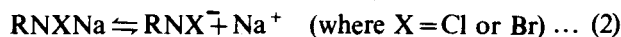
Table 5—Calculated Constants of the Rate-Determining Steps as Functions of Temperature and Dielectric Constant

Temp (K)	10 <sup>4</sup> k <sub>calc.</sub> (s <sup>-1</sup> )	
	CAB	BAB
293	—	19.9
303	5.5	41.7
313	32.8	87.7
323	384.5	—
Dielectric constant		
76.58	11.1	—
74.33	—	53.1
72.08	20.0	64.6
67.59	33.0	106.8
58.61	200.0	—

\* k<sub>calc.</sub> = k<sub>2</sub>(CAB), k<sub>3</sub>(BAB); for k<sub>2</sub> and k<sub>3</sub> see Eqs (8) and (11).

#### Discussion

Both chloramine-B and bromamine-B are fairly strong electrolytes in aqueous solutions<sup>8,12,13</sup>. The following equilibria exist in their solutions:

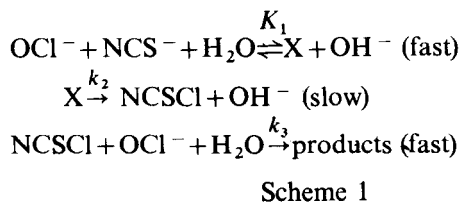


$$[K_a = 3.3 \times 10^{-8} (\text{HOCl}); 2 \times 10^{-9} (\text{HOBr}) \text{ at } 25^\circ\text{C}]$$

Hence the probable reactive species in the alkaline solutions of CAB and BAB, depending upon the pH of the medium are RNHX, RNX<sup>-</sup>, HOX and OX<sup>-</sup>, X being Cl or Br. After pH 3 [RNX<sup>-</sup>] > [RNHX] and

upto pH 10  $[RNHX] > [HOX]$ , and thereafter  $[HOX] > [RNHX]$ . Above pH 9  $[OX^-] \gg [RNHX]$  or  $[HOX]$ .

**Mechanism of oxidations:** (1) *With chloramine-B*—In the oxidation of  $NCS^-$  by CAB first order in  $[CAB]_0$ , fractional order in  $[NCS^-]$  and inverse fractional order in  $[OH^-]$  may be explained by Scheme 1,



Based on Scheme 1, the rate law is given by Eq. (7)

$$\frac{-d[CAB]}{dt} = \frac{K_1 k_2 [CAB]_T [NCS^-] [H_2O]}{[OH^-] + K_1 [NCS^-] [H_2O]}$$

or

$$k_{obs} = \frac{K_1 k_2 [NCS^-] [H_2O]}{[OH^-] + K_1 [NCS^-] [H_2O]} \quad \dots (7)$$

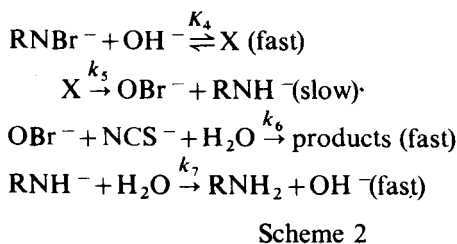
or

$$\frac{1}{k_{obs}} = \frac{[OH^-]}{K_1 k_2 [NCS^-] [H_2O]} + \frac{1}{k_2} \quad \dots (8)$$

The plots of  $1/k_{obs}$  versus  $[OH^-]$  (Fig. 1) and  $1/k_{obs}$  versus  $1/[NCS^-]$  (Fig. 1) were linear with the same intercept in accordance with the rate law (8). The equilibrium constant ( $K_1$ ) and the disproportionation constant ( $k_2$ ) have been computed from the slope and intercepts of the plots ( $K_1 = 1.09 \times 10^{-5}$ ,  $k_2 = 2.04 \times 10^{-3} s^{-1}$  at higher [substrate]).

(2) *With bromamine-B*

Schem 2 and rate law (9) account for the observed results of first order in  $[BAB]$ , fractional order in  $[OH^-]$  and zero order in  $[NCS^-]$ .



$$\frac{-d[BAB]}{dt} = \frac{K_4 k_5 [BAB]_0 [OH^-]}{1 + K_4 [OH^-]} \quad \dots (9)$$

or

$$k_{obs} = \frac{K_4 k_5 [OH^-]}{1 + K_4 [OH^-]} \quad \dots (10)$$

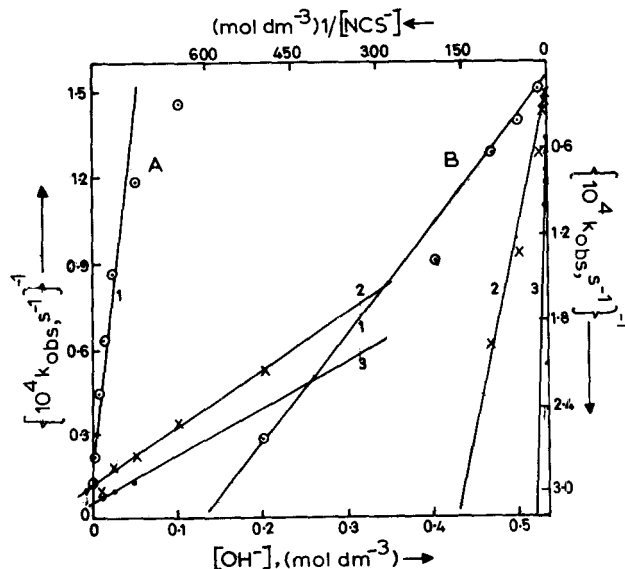


Fig. 1—(A) Plot of  $1/k_{obs}$  versus  $[OH^-]$  ((1)  $10^3[CAB] = 0.5 \text{ mol dm}^{-3}$ ,  $10[NCS^-] = 0.1 \text{ mol dm}^{-3}$ ,  $T = 313 \text{ K}$ . (2)  $10^3[CAB] = 1.0 \text{ mol dm}^{-3}$ ,  $10[NCS^-] = 1.0 \text{ mol dm}^{-3}$ ,  $T = 313 \text{ K}$ . (3)  $10^3[CAB] = 5.0 \text{ mol dm}^{-3}$ ,  $10[NCS^-] = 5.0 \text{ mol dm}^{-3}$ ,  $T = 303 \text{ K}$ ) (B)—Plot of  $1/k_{obs}$  versus  $1/[NCS^-]$  ((1)  $10^3[CAB] = 0.5 \text{ mol dm}^{-3}$ ,  $10^2[OH^-] = 1.0 \text{ mol dm}^{-3}$ ,  $T = 313 \text{ K}$ . (2)  $10^3[CAB] = 1.0 \text{ mol dm}^{-3}$ ,  $10^2[OH^-] = 10.0 \text{ mol dm}^{-3}$ ,  $T = 313 \text{ K}$ . (3)  $10^3[CAB] = 5.0 \text{ mol dm}^{-3}$ ,  $10^2[OH^-] = 2.5 \text{ mol dm}^{-3}$ ,  $T = 303 \text{ K}$ )

or

$$\frac{1}{k_{obs}} = \frac{1}{K_4 k_5 [OH^-]} + \frac{1}{k_5} \quad \dots (11)$$

$1/k_{obs}$  versus  $1/[OH^-]$  (Fig. 2) was linear in conformity with rate law (11). The slope and intercept gave the formation constant  $K_4$  and decomposition constant  $k_5$  ( $K_4 = 4.41$ ; and  $k_5 = 0.01 s^{-1}$ ).

The observed increase in rate with decrease in dielectric constant of the medium can be accounted by Laidler and Eyring equation<sup>14,15</sup>

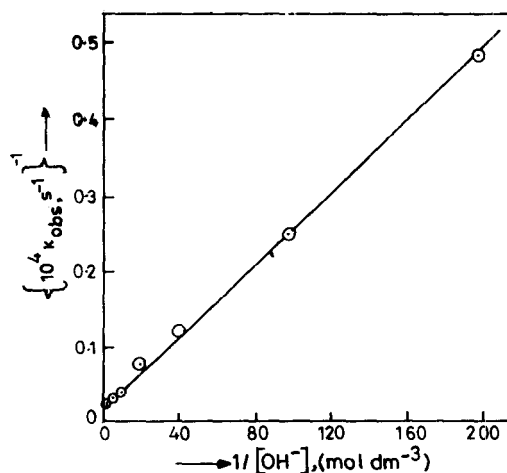


Fig. 2—Plot of  $1/k_{obs}$  versus  $1/[OH^-]$  ( $10^3[BAB] = 5.0 \text{ mol dm}^{-3}$ ,  $10[NCS^-] = 1.0 \text{ mol dm}^{-3}$ ,  $T = 303 \text{ K}$ ;  $\mu = 0.5 \text{ mol dm}^{-3}$ )

$$\ln k = \ln k_0 + \frac{e^2}{2DkT} \left[ \frac{1}{r} - \frac{1}{r^\ddagger} \right] \quad \dots (12)$$

where  $k$ 's are the rate constants and  $r$ 's the radii of the reactant species and activated complex. It is evident from Eq. (12) that the rate is greater in a medium of lower dielectric constant when  $r^\ddagger > r$ . In the present investigations, it is quite likely that the radius of the activated complex is greater than the radii of reactants as the rate determining step involves the interaction between negative ions.

It can be concluded from the examination of kinetic data and above discussion that BAB is more powerful oxidant than CAB in the alkaline medium.

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