Analysis of Complex Species Produced by the Szillard-Chalmers Process from Hexaquo-chromium Chloride $Cr(H_2O)_6Cl_3$ and Tetraquo-chromium Chloride $[Cr(H_2O)_4Cl_2]\cdot Cl\cdot 2H_2O$

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Radioactive ^{51}Cr compound of a high specific activity can easily be obtained in a reactor by the Szillard-Chalmers process, using as a target an inner complex salt of chromium[1]. For example, Harbottle et al.[2] obtained hexavalent chromate or bichromate salt with a retention value of more or less 90%, depending on the nature of the counter-cation. They also obtained similar retention values for several trivalent chromium compound. In our present work, the retention of the chromium aquo-complex was investigated with a view to finding the way the energy of radioactive recoil is dissipated under the influence of a complex ligand field. Two different kinds of chromium chloride isomers were used as targets in this work, and neutron irradiation was effected in the JRR-1 reactor of the Japan Atomic Energy Research Institute. The activated products were separated into several portions of complex species by ion-exchange chromatography, and two samples of the separated portions were put into radiometric analysis for determining the ^{51}Cr yields and into colorimetric analysis for determining the total chromium content.

Experimental

Preparation of Chromium Complex.—Hexaquo- (purple) and tetraquo- (green) chloride complex salts were prepared by the method described in "Inorganic Synthesis"[4]; confirmation of the

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[1] N. Shibata and K. Yoshihara, This Bulletin, 32, 422 (1959)

[2] G. Harbottle, *J. Chem. Phys.*, **22**, 1083 (1954); A. G. Maddock et al., *Nature*, **164**, 788 (1949).

[3] J. W. Cobble and G. E. Boyd, *J. Am. Chem. Soc.*, **74**, 248 (1952).

[4] Ed. by T. Inoue, Y. Tsunoda and T. Takeuchi, "Inorganic Preparation", Conference of Complex Chemistry in Japan, No. 202 (November 23, 1959).

purity was made with a Beckman D. U.-type spectrophotometer using the salts absorption spectra. Two pure stable salts of chromium chloride isomers were obtained; however, they could not be stored, even in a sulfuric acid desiccator, without partial degradation. It was found that the one isomer changed into the other by the degradation, even at room temperature. For obtaining the net yield of the radiolytic decomposition of the Szillard-Chalmers reaction, we must know the yield of natural degradation, probably caused by thermal and photochemical reactions, as a function of the time elasped before irradiation.

Irradiation.—The irradiation was effected in a closed silica or polyethylene tube containing several grams of silica gel, which was used as a desiccating agent. For neutron irradiation the target sample was placed in the No. 12 hole of JRR-1, which provided a thermal neutron flux of 2×10^{11} n/cm^2/sec. together with a γ flux of 4.5×10^5 r/hr. For γ irradiation, the sample was placed 20 cm. apart from the ^{60}Co source of 1000 curie in the Radiochemical Laboratory, the Institute of Physical and Chemical Research; this provided a dose rate of 4.5×10^4 r/hr.

Separation of Complex Species.—About 0.1 mequiv. weight of the target chromium complex was dissolved in thrice-distilled water, and the 0.1 M solution thus prepared was passed through a cation-exchange resin column 1.5 cm. in diameter and 15 cm. in length, with 12 g. of air-dried Amberlite IR-120. Then, the resin column was washed successively with water, 0.05 N perchloric acid, a 0.05 N sodium hydroxide solution, and 2 N hydrochloric acid. These eluants, proposed by Gustavson and Kawamura⁶⁾, permitted us to separate the complex species in the order given below:

Chromate, tetraquo-dichloro chromim (III), pentaquo-monochloro chromium (III) and hexaquo chromium (III) complex.

Colorimetry of the Total Chromium.—The solutions of each effluent from the cation-exchange resin column were made alkaline with 0.2 N sodium hydroxide, and the resulting alkaline solutions were treated with hydrogen peroxide in order to convert chromium (III) into chromium (VI). The developed yellow color was measured with a Beckman D.U.-type spectrophotometer⁷⁾.

Radioactivity Measurement.—After cooling for two weeks, the neutron-irradiated sample was dissolved in a small quantity of water. Then, the species of the chromium complex tagged with radioactive ^{51}Cr were separated by ione-xchange chromatography. For measuring the radioactivity due to ^{51}Cr in the separated fractions, a given amount of inactive chromium (III) salt was added as a carrier: this provided uniform precipitates of a given thickness for radioactive assay. Chromium (III) was converted into hexavalent chromate by oxidation with hydrogen peroxide in an alkaline medium, and lead chromate was precipitated. The yellow precipitates of lead chromate, containing ^{51}Cr, were filtered off, dried and mounted for radioactivity measurement. A bell-type G. M. counter was generally used for the activity measurement, but a dipping-type counter with a wall thickness of 37 mg./cm^2 was also used when simultaneous determinations of the total and of the radioactive chromium were needed. The main radioactive impurity was ^{35}S, produced by (n, p) reaction from ^{35}Cl in chromic chloride. This interference could be avoided by absorbing the soft β rays with an aluminum absorber 8.9 mg./cm^2 thick. The radioactive ^{32}P, even if produced by a fast neutron by a (n, α) reaction with an cross section of 0.13 barn, did not interfere with our measurement of ^{51}Cr, because anionic phosphate could be eliminated during the chemical separations by cation-exchange resin and by precipitation. Actually, ^{32}P was not detected in such an amount as to affect the determination of ^{51}Cr.

Results

Separation and Recovery by Ion-exchange Chromatography.—A synthetic mixture of pure tetraquo- and hexaquo-complex salts was dissolved in water to produce a 0.2 M solution with regard to each component, and the complex species were adsorped on a hydrogen-form cation-exchange resin column. The separation was effected by the eluants as described above (Experimental). The elution chromatogram in Fig. 1 shows the quantitative recovery of two isomers.

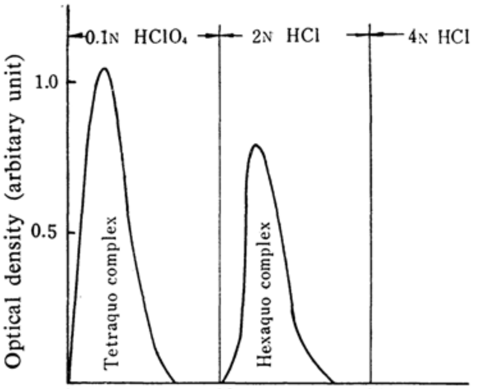

Fig. 1. Elution curve of a mixture of tetraquo- and hexaquo-complex.

Radioactive Species.—The yields of radioactive chromium complex species produced by neutron activation were determined radiochemically after separaion by ion-exchange chromatography. Each 5 ml. portion of the effluents was taken for counting the radioactivity in the course of the elution. The results of the measured radioactivity and the calculated enrichment factors are presented in Fig. 2.

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5) M. Kondo, The First Conference of Utilisation of Radioisotopes in Japan (1957).

6) K. H. Gustavson, *Sv. Kem. Tid*, **56**, 14 (1944); R. Kawamura, *Jap. Analyst*, **4**, 277 (1955).

7) E. B. Sandell, "Colorimetric Determination of Traces of Metals", New York (1950), p. 388.

TABLE I. γ-RAY DECOMPOSITION AND NATURAL DEGRADATION YIELD OF TETRAQUO-DICHLORO COMPLEX SALT (A) AND HEXAQUO-COMPLEX SALT (B)

Decomp. products opt. dens./100 ml.	i) Neutron and γ in a pile	ii) γ from ^{60}Co	iii) Natural degradation
A)			
Sample taken	0.204 (100%)	0.222 (100%)	0.283 (100%)
H_2O fraction (neutral and anionic)	0.000 (0%)	0.000 (0%)	0.000 (0%)
0.1 N $HClO_4$ fraction (tetraquo)	0.265 (94.5%)	0.202 (91%)	0.186 (91%)
HCl fraction (hexaquo)	0.028 (10%)	0.028 (7%)	0.018 (9%)
Summation deviation	0.010 (−4%)	0.004 (2%)	0.000 (0%)
B)			
Sample taken	0.360 (100%)	0.247 (100%)	0.286 (100%)
H_2O fraction (neutral and anionic)	0.012 (3%)	0.000 (0%)	0.005 (2%)
0.1 N $HClO_4$ (tetraquo)	0.042 (12%)	0.070 (28%)	0.051 (18%)
HCl fraction (hexaquo)	0.275 (77%)	0.172 (70%)	0.211 (74%)
Summation deviation	0.028 (8%)	0.005 (2%)	0.009 (7%)

The first effluent of the ion-exchange chromatograms contains unknown neutral and anionic species. The second activity peak in Fig. 2 indicates the presence of tetraquo-dichloro chromium-51, corresponding to the Szillard-Chalmers retention value. Similarly, the third peak shows the eluted pentaquo-monochloro chromium-51. The last effluent, obtained by a hydrocholoric acid stronger than 2 N, is ascribed to the hexaquo chromium-51 fraction according to the results of the preliminary test on the ion-exchange chromatography. The observed specific activities or enrichment factors of the first and third peaks were nearly the same, but each was a hundred times as large as that of the second. This is because of the partial degradation of the tetraquo-complex into the hexaquo-complex during the times of irradiation and storage. Besides, the treatment with a 0.05 N sodium hydroxide solution for eluting pentaquo-complex species causes a sort of degradation of the hexaquo-complex in the resin phase, forming a species which can not easily be eluted with 2 N hydrochloric acid. The effect of the natural degradation of the tetraquo-complex target on the yield of radioactive complex species can be clearly seen in Table I; and the similar effect of pretreatment with 0.05 N sodium hydroxide is shown in Table II.

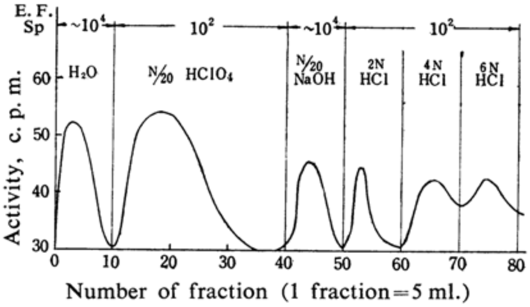


Fig. 2. Distribution of decomposition products by neutron-irradiated tetraquo-complex.
Sp; Specific activity (activity/optical density)
E. F.; Enrichment factor

TABLE II. PERCENT YIELD OF ^{51}Cr BY THE ELUTION WITH HCl MORE THAN 2 N. COMPARISON WAS MADE BETWEEN THE YIELDS WITH AND WITHOUT PRETREATMENT USING 1/20 N NaOH

Treatment	Eluant	
	4 N HCl	6 N HCl
Yield with treatment	17%	12%
Yield without treatment	less than 3%	less than 3%

It is supposed that an unstable chlomium complex in a valency state higher than three might be produced by neutron activation and that the absorption of this species on the resin is too strong to be eluted with 2 N hydrochloric acid. If chromium(IV) or chromium(V) were formed in the irradiated sample, then the chloride of chromium trichloride would act as a reducing agent against chromium(IV) or chromium(V) which is probably a powerful oxidizing agent. For this reason, an elution was carried out with 2 N hydrochloric acid in the presence of excess sulfurous acid, but no appreciable change was observed in the elution characteristics; the conclusion was drawn that there was no chromium(IV) or chromium(V).

Radioactive Complex Species Produced from the Hexaquo- and Tetraquo-complex Target.— The yield of radioactive chromium complex species produced by neutron activation from two different targets, the hexaquo- and tetraquo-complex isomers, is presented in Figs. 3 and 4. Beside these, the amount of chromium found in each fraction of chromatograms, as

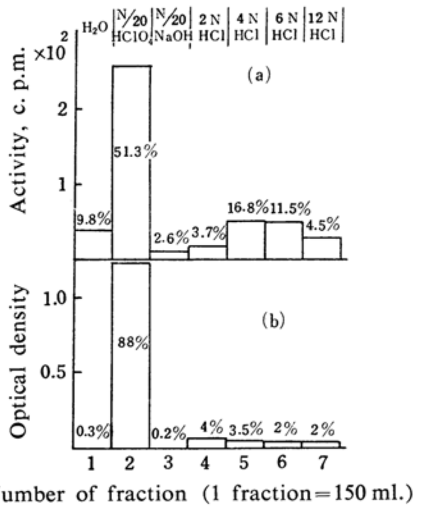


Fig. 3. Irradiated tetraquo-complex.
(a) Comparison of the amount of ^{51}Cr (expressed in radioactivity), (b) the amount of the total chromium (expressed in optical density) in the sample.

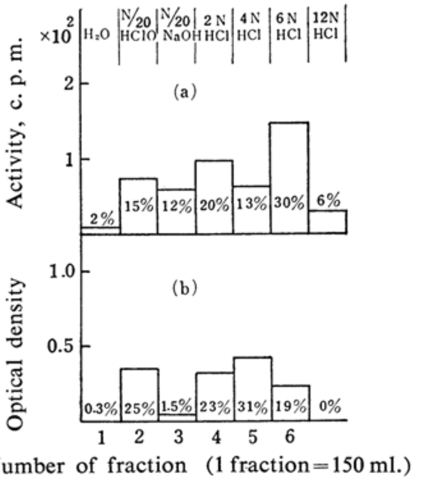


Fig. 4. Irradiated hexaquo-complex.
(a) Comparison of the amount of ^{51}Cr (expressed in radioactivity), (b) the amount of the total Cr (expressed in optical density) in the sample.

determined by colorimetric analysis, is shown in Figs. 3 and 4.

As the hexaquo-complex is much more labile than the tetraquo-complex, not only to radiation decomposition but also to natural degradation in air, the contribution of the latter effect must be considered in order to obtain the correct yield of the radiation decomposition of the hexaquo-complex. However, this effect is so small for the tetraquo-complex that the correction is not necessary. The corrected yields for the radioactive chromium species are shown in Fig. 5 for the hexaquo-chromium target and in Fig. 3 for the tetraquo-chromium target.

Anionic Species of the Activated Chromium Complex.—The first effluent produced by exchange chromatography was passed through a column filled with anion-exchange resin, Dowex 1-X8. Less than 8% of the radioactive chromium was adsorbed on the anion-exchange resin. Therefore, the remaining 92% is considered to be present in a non-ionic form, but the chemical species of the latter was not identified. As to the anionic species, the extraction of chromium as perchromic acid by ethyl acetate was undertaken from acetic acid and a sodium acetate buffer solution at pH 1.6 in order to prove the presence of the chromate anion. The extracted radioactivity was less than 5% of the total present in the first effluent produced by cation-exchange chromatography.

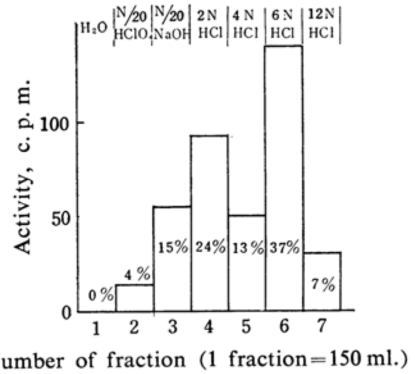


Fig. 5. Corrected distribution of ionic species for neutron irradiated hexaquo-complex.

Discussion

The yields of complex species of radioactive chromium(III) are summarized in Table III. As the retention values for two different isomers differ greatly from one another, we

TABLE III. SUMMARY OF YIELD

Decomp. product	Yield, %			
	$[Cr(H_2O)_4Cl_2]\cdot Cl\cdot 2H_2O$ target %		$[Cr(H_2O)_6]Cl_3$ target %	
Anionic ^{51}Cr salt	2			
Neutral ^{51}Cr salt	8			
Tetraquo ^{51}Cr salt	50			
Pentaquo ^{51}Cr salt	3		15	
Hexaquo ^{51}Cr salt	4			
Eluant by 2 N HCl	4	37	24	80
4 N HCl	17		13	
6 N HCl	12		37	
12 N HCl	4		7	
Retention	50		80	

hoped from stereochemistry of the complex to get some information about the energy dissipation of the recoil chromium atom under the influence of the ligand field. The energy liberation by the process $^{50}Cr(n, \gamma)^{51}Cr$ was evaluated to be 9.2 MeV. from the atomic mass difference between ^{50}Cr and ^{51}Cr. From this, the recoil energy imparted to the ^{51}Cr atom by the emission of γ rays is estimated to be 839 eV. This energy must be imparted to the surrounding ligand atoms in different ways depending on the geometrical arrangement of the ligand in the chromium chloride complex. The actually observed Szillard-Chalmers effect is not the same with respect to the yield of the radioactive chromium complex for the two different isomers, hexaquo- and tetraquo-chromium chloride.

As the positively charged (+3e) recoil chromium atom is so heavy compared to the surrounding ligand atoms, the former can not escape from the interior of the crystal without any interaction. First, we suppose the recoil energy is imparted equally to three ligand atoms on the same plane of the octahedral surface; therefore these atoms will be expelled out of the complex crystal and caught by some interstitial site of the crystal. The radioactive recoil chromium atom will then recombine by statistical chance with an atom or a water molecule at the nearest neighbor's forming a certain species of the complex. As six water molecules and three chloride ions are the nearest neigbors in the present case, the yield of the radioactive complex species can be ruled out by simple statistics. With this assumption, the radioactive chromium complex yields must be 2/10 for the formation of the hexaquo-complex species, 3/10 for that of the pentaquo-complex, and 2/10 for that of the tetraquo-complex, regardless of the target complex. However, this hypothesis can not account for the experimental results shown in Table IV.

TABLE IV. COMPARISON OF THE SZILLARD-CHALMERS YIELD OF CHROMIUM CHLORIDE COMPLEX WITH THE THEORETICAL YIELD BASED ON COMPLETE DISSOCIATION AND STATISTICAL REARRANGEMENT OF LIGAND ATOMS

Target complex	Tetra isomer	Hexa isomer	Theoretical
Product		yield, %	
Tetra form	50 (Retention)	4	28.5
Penta form	3	15	43
Hexa form	37	80 (Retention)	28.5

Secondly, the whole energy is transferred to one special ligand atom by head-on collision, and the kinetic energy of the recoil atom is effectively absorbed by this ligand atom. If the recoil energy is not greater than the binding energy between the central metal ion and the ligand atom, the retention value can be estimated as follows. The binding energy of one ligand water molecule to the central chromium atom is estimated to be 48/6 = 8 eV. from the hydration energy of the chromium ion. However, this value must be multiplied by the factor of M°/M, for the available energy for bond-breaking is smaller than the recoil energy by this factor since momentum partition between the water molecule and the recoil chromium atom takes place. Therefore, the minimum energy is $8\times(159/18)=70.6$ eV. for breaking one ligand bond. The energy, required to remove successively one more ligand water amounts to $70.6\times(141/18)=555$eV. From this consideration, the recoil atom having less energy than this threshold energy of 70.6 eV. must retain its initial ionic form of the complex. Similarly, in the recoil chromium atom having between 70.6 and 555 eV. of energy the yields of radioactive chromium complex are different in ligand number by one from the initial form of the target complex. In the case of the tetraquo-complex as the terget the energy necessary to remove one chlorine atom from the complex crystal field can be estimated from the absorption spectroscopic data to be one-half of the energy needed for the water molecule. However, the reduction factor of the available energy for bond-breaking, M/M°, is twice as large as that of the water molecule. Therefore, the threshold energy for breaking the ligand chlorine bond is nearly one-fourth that of the evaluated energy for ligand water.

The Effect of the Multicascade of γ Emission.—The calculation of the recoil energy is not so simple as has been discussed above, since γ emission in the neutron gamma process generally takes place through several steps in cascade. In this discussion, we treat the problem as if γ emission occurred in two steps, since the final result does not differ essentially from that of multicascade emission. Assuming that successive γ photons of the same energy are emitted in two directions with an angle α, we can expect the relation between the recoil energy with no cascade, E°, and with a two-steps cascade, E', given by the Eq. 1:

$$E' = E^\circ \cos^2(\alpha/2) \qquad (1)$$

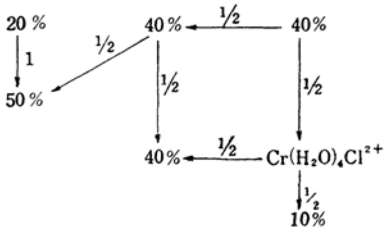
As successive γ emission takes place in a random direction, the angle α divided by π gives a probability of the event where a successive γ emission occurs between 0 and α. In Fig. 6 the α/π value is plotted against the

TABLE V. THE EFFECT OF MULTICASCADE γ EMISSION ON THE SZILLARD-CHALMERS REACTION YIELDS. THE TENTATIVE CALCULATION OF THE YIELDS FOR RECOIL INTERMEDIATES AND FINAL PRODUCTS WAS BASED ON THE SPATIAL RECOIL ENERGY DISTRIBUTION BY TWO SUCCESSIVE γ EMISSION

a) Hexaquo-dichloro complex target

Recoil process	Zero ligand dissociation	One ligand dissociation	Two ligand dissociation
Threshold energy	less than 70.5 eV.	70.5 eV.	555 eV.
Assumed species and its initial yield	$Cr(H_2O)_6^{3+}$	$Cr(H_2O)_5^{3+}$	$Cr(H_2O)_4^{3+}$

Products and its observed yield



$Cr(H_2O)_6^{3+}$ (80%)

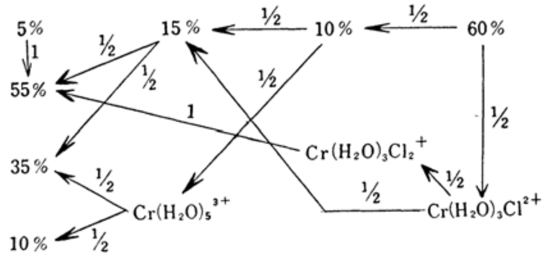
$Cr(H_2O)_5Cl^{2+}$ (15%)

$Cr(H_2O)_4Cl_2^{+}$ (4%)

b) Tetraquo-dichloro complex target

Recoil process	Zero ligand dissociation	One ligand dissociation	Two ligand dissociation	Three ligand dissociation
Threshold energy	less than 17.6 eV.	17.6 eV.	70 eV.	more than 280 eV.
Assumed species and its initial yield	$Cr(H_2O)_4Cl_2^{+}$	$Cr(H_2O)_4Cl^{2+}$	$Cr(H_2O)_4^{3+}$	$Cr(H_2O)_3^{3+}$

Products and its observed yield



$Cr(H_2O)_4Cl_2^{+}$ (50%)

$Cr(H_2O)_5Cl^{2+}$ (3%)

$Cr(H_2O)_6^{3+}$ (37%)

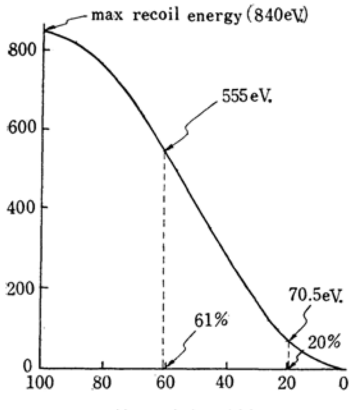


Fig. 6. Recoil energy of ^{51}Cr calculated from Eq. 1 vs. $(1-\alpha/\pi)\times 100$ which represents percentage of ^{51}Cr having recoil energy E'.

recoil energy, E', for a two-cascades emission of γ rays by the aid of Eq. 1. Taking the threshold energy value, E', for bond-breaking, we can determine the probability, α/π, from the curve shown in Fig. 6, which gives the yield of the complex species of radioactive chromium produced by neutron-gamma reaction. The α/π fraction for the given threshold, E', insufficient to break one bond, gives the retention yield of radioactive chromium. Similarly, the α/π value for the threshold corresponding to the breaking of two or more bonds, gives the yield of the complex species of radioactive chromium differing by one or more ligand atom. An intermediate complex, lacking one or more ligand atom, reproduces a normal six-ligand complex species by picking up either a water molecule or a chlorine atom depending on the relative abundance of the surrounding ligand species. For example, an intermediate $Cr(H_2O)_5^{3+}$ will reproduce either one of two stable complex six-ligand species, $Cr(H_2O)_5^{3+}$ or $Cr(H_2O)_6Cl^{2+}$, with equal probability. Therefore, on the basis of the above assumption, the final products of the radioactive chromium complex can be estimated; the schemata are presented in Table Va for a hexaquo target and in Table Vb for a tetraquo target.

The tables show that double γ emission schema plausibly improve the agreement between the calculated and observed results more than the simple cascade scheme does.

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