constant for the net reaction; it predicts a specific rate at 25° of $10^{-2}\ M^{-1}\ \text{sec.}^{-1}$. Although the observed rate is ~60 times higher, this may be due to the present suggested mechanism for electron transfer, which is entirely different from the outer-sphere process assumed in the theory. The present study does not provide a check on any of the premises of the Marcus theory. Since the outer-sphere path has a predicted rate lower than that observed, it also does not refute the theory in any way.

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Kinetics of the Reduction of Halopentaamminecobalt(III) Complexes by Iron(II) and Vanadium(II)

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The rates at which the complex ions $(NH_3)_5CoF^{2+}$, $(NH_3)_5CoCl^{2+}$, and $(NH_3)_5CoBr^{2+}$ react with Fe^{2+} are strictly first order in each of the reactants. At 25.5° and $\mu = 1.7$, the corresponding specific rates k_0 are 76×10^{-4}, 16×10^{-4}, and 9.2×10^{-4} M^{-1} sec.$^{-1}$. The respective values of ΔH^* are 13.4, 14.5, and 15.6 kcal. mole^{-1} and of ΔS^* are −23, −23, and −20 e.u. The reactions are accelerated by free halide in solution and this acceleration can be expressed by the rate term $k_1(Fe^{2+})\cdot(\text{complex}^{2+})(X^-)$. With $(NH_3)_5CoF^{2+}$ as reactant $k_1 = 3.5 \pm 1 \times 10^{-3}$, $2.1 \pm 0.2 \times 10^{-2}$, and $13 \pm 2\ M^{-2}$ sec.$^{-1}$ for $X^- = Br^-$, Cl^-, and F^-, respectively; with $(NH_3)_5CoBr^{2+}$, $k_1 \leq 1 \times 10^{-3}\ M^{-2}$ sec.$^{-2}$ for $X^- = Cl^-$ and $4 \pm 1\ M^{-2}$ sec.$^{-1}$ for $X^- = F^-$ (temperature 25.8 ± 0.2°, $\mu = 1.7$ except for $X^- = F^-$; here the temperature was 25.1 ± 0.1°, $\mu = 2.0$).

This paper presents the results of kinetic studies on the reduction of complexes of the type $[(NH_3)_5CoX]^{2+}$, where X = F, Cl, or Br, by Fe^{2+}(aq) and V^{2+}(aq). The investigation was started originally as part of a somewhat wider program, aimed especially at getting more information on the nature of the activated complex in such electron-transfer reactions by indirect means based on rate comparisons.[1] The investigation was discontinued, however, after the manuscript of a paper now published by Candlin, Halpern, and Trimm[2a] became available dealing with much the same subject and in closely related systems. Our results, however, do seem worth reporting because they are new[2b] and do contribute to the knowledge in this field.

Experimental

Materials.—The Co(III) complexes were used in the form of their perchlorates, $[(NH_3)_5CoCl](ClO_4)_2$ and $[(NH_3)_5CoBr](ClO_4)_2$, which were prepared according to published procedures.[3]

Fluoropentaamminecobalt(III) perchlorate was precipitated from a solution of $[(NH_3)_5CoF](NO_3)_2$, which had been prepared according to a description by Basolo and Murmann.[4] A concentrated solution of sodium perchlorate was used for the precipitation (perchloric acid in high concentration catalyzes the aquation of the complex). The purity of the complex compounds was checked spectrophotometrically. Ferrous perchlorate was obtained from the G. F. Smith Chemical Co. and purified by recrystallization from $HClO_4$. A stock solution of the compound was kept in the dark under nitrogen and standardized from time to time by titration with cerium(IV) sulfate using ferroin as indicator. A solution of V^{2+} was prepared by reduction of a suspension of V_2O_5 (Baker Analyzed Reagent) in $HClO_4$ solution with amalgamated zinc. The V^{2+} solution was standardized spectrophotometrically, using its reduction capacity on a $[(NH_3)_5CoCl]^{2+}$ solution of defined concentration. Sodium perchlorate, which was used to adjust the ionic strength, was prepared from sodium carbonate and perchloric acid.

Chemicals other than the ones mentioned are of the best quality commercially available and were used without further purification.

The reagent solutions were prepared with twice-distilled water.

Procedure.—Great care was exercised to exclude air from the deoxygenated reactant solutions during the mixing procedure and the reaction.

The oxidation–reduction reaction was followed spectrophotometrically, using the absorption maximum of the Co(III) complexes in the visible range for observation. The measurements were carried out with a Cary Model 14 spectrophotometer, the cell compartment of which was thermostated to an accuracy of ±0.1–0.2°. In general a cell of 5-cm. path length was used for the studies. The reductions by Fe^{2+} are slow enough so that large concentrations of this reagent can be used. The reactions were run with (Fe^{2+}) in the range 0.15 to 0.6 M and (Co(III)) about $3 \times 10^{-3}\ M$, thus providing pseudo-first-order kinetic conditions.

Results and Discussion

Reduction by V^{2+}.—The reactions between V^{2+} and the Co(III) complexes were found to be first order in both reactants. The rate law can then be represented as

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(1) A. M. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

(2) (a) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964). (b) This is strictly true only of the experiments on the halide-assisted reaction. Concurrently with this work, Dr. J. Espenson of Iowa State University measured the rates of reaction of Fe^{+2} with halopentaamminecobalt(III) complexes. His rates at $\mu = 1.00$ and 25° are about 15% smaller than ours at $\mu = 1.7$. See *Inorg. Chem.*, **4**, 121 (1965).

(3) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

(4) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 172 (1953).

$$\log \frac{1 - \dfrac{a}{b}\dfrac{A_0 - A_t}{A_0 - A_\infty}}{1 - \dfrac{A_0 - A_t}{A_0 - A_\infty}} = \frac{b - a}{2.30} kt \qquad (1)$$

where a and b are the initial concentrations of the reactants and A_0, A_t, and A_∞ stand for the absorbancy at the time zero, the time t, and after the reaction has gone to completion. The rate constants were obtained from the slope of the straight lines which result when the expression on the left-hand side of eq. 1 is plotted *vs.* the time.

A summary of our results for the V^{2+}–Co(III) reactions is shown in Table I. The first two values of Table I agree fairly well with those reported recently[2] for very similar conditions, but there is a discrepancy in the rate constants for the reaction involving the bromo complex. The meager variation in k which results from a change of the complex ligand X has been pointed out previously and the suggestion has been made that the reactions with V^{2+} proceed by an outer-sphere activated complex.[1,2]

TABLE I

REDUCTION BY V^{2+} OF HALOPENTAAMMINECOBALT(III)COMPLEXES[a]

Reaction	k, M^{-1} sec.$^{-1}$	
$V^{2+} + [(NH_3)_5CoF]^{2+}$	2.9	(2.6)[b]
$V^{2+} + [(NH_3)_5CoCl]^{2+}$	5.6	(~5)[b]
$V^{2+} + [(NH_3)_5CoBr]^{2+}$	14.6	(25)[b]

[a] Temperature 22.5 ± 0.5°; $\mu = 0.52$; $[H^+] = 0.5$ M. Range of $(V^{-2})_0$, 1.2×10^{-3} to 2.4×10^{-3} M; range of $(Co(III))_0$, 1.6×10^{-3} to 3.3×10^{-3} M. [b] Values in parentheses are from ref. 2.

Reduction by Fe^{2+}.—Over the concentration range 0.15 to 0.6 M in $Fe(ClO_4)_2$, μ being held constant using $NaClO_4$, the second-order specific rates were found to be constant within 3% and thus we conclude that the reactions are first order in Fe^{2+}. Each individual run under pseudo-first-order conditions provides an opportunity for establishing the order with respect to Co(III), within the concentration range investigated. In every case, pseudo-first-order behavior was observed over at least four half-lives, and more often over five. The deviations toward the end of an experiment were never outside of experimental error. The variation of k with acid concentration was also studied over the range 0.1 to 0.9 M in $[H^+]$ and we concluded that the rate is independent of this variable in this range. Actually, a small increase in k for the reaction of $(NH_3)_5CoF^{2+}$ with Fe^{2+} with acidity was noted when H^+ was substituted for Na^+ in the solution. However, substitution of Li^+ for Na^+ produced an effect almost as large and we therefore concluded that we were observing an ion atmosphere effect rather than a specific effect of acidity. The data pertaining to this point are as follows. For a medium 0.1 M in H^+ and 0.84 M in Na^+, k is 7.1×10^{-3} M^{-1} sec.$^{-1}$; for 0.10 M H^+, 0.85 M Li^+, k is 7.75×10^{-3} M^{-1} sec.$^{-1}$, and for 0.84 M H^+, 0.10 M Na^+, $k = 8.15 \times 10^{-3}$. The temperature in each case was 25.1° and $\mu = 2.0$. Studies at three different temperatures resulted in the values for the rate constants and the activation parameters shown in Table II. The values of ΔH^* and ΔS^* are of a magnitude which is quite common for electron-transfer reactions of the outer-sphere as well as of the inner-sphere type and no conclusions about mechanism can be drawn from these quantities. Less usual and quite difficult to rationalize is the observed increase in rate in the series Br^-, Cl^-, F^-. Because of the similarities of the ΔH^* values, there is no inversion of this trend up to temperatures well above 100°. Similar oxidation–reduction systems which have thus far been studied are the reactions of Cr^{2+} with CrX^{2+},[5] and with $(NH_3)_5CrX^{2+}$,[6] as well as the reduction of $(NH_3)_5CoX^{2+}$ by $Cr(dipy)_3{}^{2+}$,[7] by $Ru(NH_3)_6{}^{2+}$,[8] and by V^{2+}.[2] All reveal an increase in reactivity in the order F < Cl < Br < I. These examples include reactions known to proceed *via* bridged activated complexes and others known to react by an outer-sphere mechanism. The order of reactivity observed in these cases gave rise to the conclusion that the electron transfer is not accomplished by direct overlap of the orbitals of the two metal ions, but by means of the halide ligand as electron mediator, the heavier halide ions because of their higher polarizability being more efficient in this respect.[9] Since the completion of this work, another example of "inverse" order of reactivity has been reported,[2] the reduction of $(NH_3)_5CoX^{2+}$ by Eu^{2+}. To rationalize their observations, the authors assume that at least part of the reaction proceeds *via* a path involving a bridged activated state, and that the rate of reaction by this path increases from the iodo to the fluoro complex because of the strong increase of the standard free energy change in this direction (quantitative relationships accounting for the influence of the standard free energy change on the rate of electron-transfer reactions have been calculated[10] and confirmed experimentally[11] so far only for outer-sphere mechanisms).

TABLE II

RATES AND ACTIVATION PARAMETERS FOR THE REACTION $Fe^{2+} + (NH_3)_5CoX^{2+}$

$(H^+) = 0.3$ M; $(Fe^{2+}) = 0.47$ M; $(Co(III)) = 3 \times 10^{-3}$ M; $\mu = 1.7$

Reaction	10^4k, M^{-1} sec.$^{-1}$ 15.2°	25.5°	36.2°	ΔH^*,[a] kcal./mole	ΔS^*,[a] e.u.
$Fe^{2+} + (NH_3)_5CoBr^{2+}$	3.5	9.2	24	15.6	−20
$Fe^{2+} + (NH_3)_5CoCl^{2+}$	6.7	16	40	14.5	−23
$Fe^{2+} + (NH_3)_5CoF^{2+}$	33	76	172	13.4	−23

[a] The values of ΔH^* are estimated as accurate to within 0.6 kcal., and those of ΔS^* to within 2 e.u.

The same arguments may be applied to the case of

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(5) D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958).

(6) A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958).

(7) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

(8) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

(9) H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

(10) R. A. Marcus, *J. Phys. Chem.*, **67**, 863 (1963).

(11) R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, **3**, 1094 (1964).

reduction by Fe^{2+} because of a striking increase in the thermodynamic stability of the complexes of Fe^{3+} with X^-, as illustrated by the stability constants: $K_{FeBr^{2+}} < 0.1$,[12] $K_{FeCl^{2+}} \sim 4$,[13] $K_{FeF^{2+}} \sim 1.5 \times 10^5$.[13] Similar differences in the stability of the monohalo complexes are also encountered with Cr^{3+}, but the reduction of $(NH_3)_5CrX^{2+}$ by Cr^{2+}, which is known to occur by an inner-sphere mechanism, exhibits the "normal" reactivity pattern.[6] The apparent slight increase[14] in rate for the iron exchange reaction, $Fe^{2+} + FeX^{2+}$ from X = Br to X = F is also difficult to rationalize, since $\Delta F°$ is zero for a reaction of this type involving a bridged activated complex. Arguments of the kind presented involve tacit assumptions which in the case of the Co(III)–Fe^{2+} reactions take the form: either bond breaking in the Co(III) complexes is less important in the activated complex than bond making at the iron atom and/or the range in the values of the stability constants for the Co(III) complexes is smaller than for the Fe(III) complexes. The first assumption would be completely *ad hoc* and is at present unsupported by any other evidence. The second finds support in the values of the stability constants for the halopentaamminecobalt(III) complexes summarized by Yalman.[15] The stability constant for $(NH_3)_5CoCl^{2+}$ is less than threefold greater than that of the bromo complex at 45° and $\mu = 1.0$.

The comparisons suggest, and it is otherwise reasonable, that more than one factor may be involved in determining the relative rates for the halide complexes. An additional factor that may be important is the symmetry of the donor[16,17] and acceptor orbitals for the reacting ions. When Cr^{2+} is the reducing agent, transfer probably proceeds by means of σ interactions with the bridging ligand, but for Fe^{2+} these interactions may be of π symmetry. The sensitivity of the rates to a difference in the ligands may be much greater in the former case than in the latter, so that in the latter the effect of stronger complex formation of F^- compared to Br^- with the oxidized form of the reducing agent can become dominant.

It seemed of interest also to investigate the effect of halide ions in solution on the rate of reduction of the Co(III) complexes of Fe^{2+}(aq), since the data would be useful in comparison with those obtained for reactions of Cr^{2+} with Cr^{3+} complexes,[18] and of Cr^{2+} with Co(III) complexes.[1,19] Eventually they should be useful in understanding terms such as $(FeX^{2+})(Fe^{2+})$ in the rate laws for electron transfer in labile systems. In the present system the position in the activated complex of at least one of the X^- ions is known, it being attached to the Co(III) center.

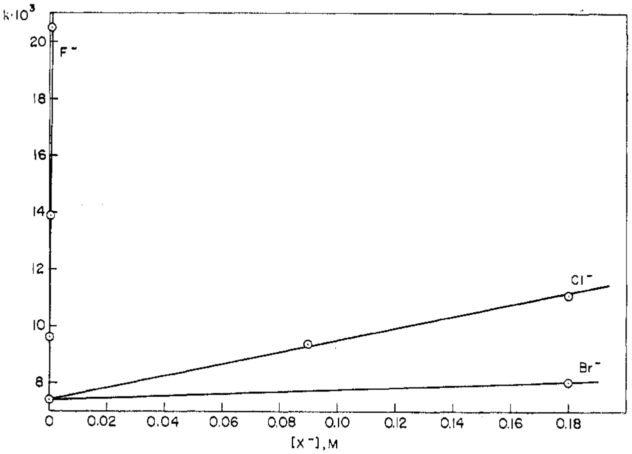

Figure 1.—Dependence of rate constant for the reaction between Fe^{2+} and $(NH_3)_5CoF^{2+}$ on the concentration of free halide ions.

Experimental results showing the effect of F^- or Cl^- on the rate at which Fe^{2+} reacts with $Co(NH_3)_5^{2+}$ are shown in Figure 1. The complete rate law covering also the effect of free X^- on the rate takes the form

$$R = (k_0 + k_1[X^-])[(NH_3)_5CoF^{2+}][Fe(II)]$$

The parameter k_0 has already been determined (last line of Table II), while for the rate constant of the ligand-assisted path when $(NH_3)_5CoF^{+2}$ is the oxidizing agent we find: $k_1 = 3.5\ (\pm 1) \times 10^{-3}\ M^{-2}$ sec.$^{-1}$ for X = Br; $k_1 = 2.1\ (\pm 0.2) \times 10^{-2}\ M^{-2}$ sec.$^{-1}$ for X = Cl; $k_1 = 13 \pm 2\ M^{-1}$ sec.$^{-1}$ for X = F. (For X = Br and Cl, $T = 25.8 \pm 0.2°$, $\mu = 1.7$, $[H^+] = 0.19\ M$. For X = F, $T = 25.1 \pm 0.1°$, $\mu = 2.0$, $[H^+]$ varying. Great care has to be exercised in the studies of catalysis by F^- to avoid the initial presence of Fe^{3+} in the Fe^{2+} solution, because it consumes F^- by complex formation.)

A check on the reduction of $(NH_3)_5CoBr^{2+}$ by Fe^{2+} revealed similar assisting effects of the ligands. For this reaction we found: $k_1 \leq 1 \times 10^{-3}\ M^{-2}$ sec.$^{-1}$ for X = Cl and $k_1 = 4 \pm 1\ M^{-2}$ sec.$^{-1}$ for X = F ($25.2 \pm 0.2°$, $\mu = 1.7$, $[H^+] = 0.08\ M$ for X = F and 0.2 for X = Cl). Only an upper limit for k_1 can be given in the case of Cl^- catalysis because of the low solubility of $(NH_3)_5CoBrCl_2$.

The greater effect of F^- compared to Cl^- in the two systems is qualitatively consistent with effects noted in other systems.[18,20] Again, the stabilization of Fe^{3+} by the ligand can be invoked, this stabilization being greater for F^- than for Cl^-. This, however, provides no basis for explaining why the ratio of k_1 for F^- compared to Cl^- is so different for $(NH_3)_5CoF^{2+}$ and $(NH_3)_5CoBr^{2+}$ as reactants. In the former case the ratio is 6×10^2; in the latter it exceeds 4×10^3. It is

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[12] Unpublished experiments by A. S. Wilson (Ph.D. Dissertation, University of Chicago, 1961) set the upper limit a factor of five lower than the probable value chosen, but not proven by E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).

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[18] J. B. Hunt and J. E. Earley, *ibid.*, **82**, 5312 (1960).

[19] P. V. Manning and R. C. Jarnagin, *J. Phys. Chem.*, **67**, 2884 (1963).

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possible that the distribution between inner-sphere and outer-sphere forms of the activated complexes differs for the different systems. Only after a resolution into the different components has been made can one hope to discuss the ligand effects with any degree of success.

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Contribution from the George Herbert Jones Laboratories
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Configuration Changes in the Reactions of Diazidobis(ethylenediamine)cobalt(III) Complexes with Nitrous Acid

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The reaction of nitrous acid with *cis*- or *trans*-$[Co(en)_2(N_3)_2]^+$ takes place so that in each of the cases resolution into two stages can be done with little difficulty, and the steric course in each stage can be described. *cis*-$[Co(en)_2(N_3)_2]^+$ reacts to form 77 ± 3% *cis*-$[Co(en)_2N_3H_2O]^{+2}$ and 23 ± 3% *trans*-$[Co(en)_2N_3H_2O]^{+2}$. *cis*-$[Co(en)_2N_3H_2O]^{+2}$ reacts further without change in configuration. *trans*-$[Co(en)_2(N_3)_2]^+$ reacts in the first stage with retention of configuration but *trans*-$[Co(en)_2N_3H_2O]^{+2}$ reacts to form 40 ± 5% of the *cis* diaquo product and 60 ± 5% of the *trans*. In the reaction of D-*cis*-$[Co(en)_2(N_3)_2]^+$ with excess nitrous acid there is no racemization of the product, which retains *cis* configuration.

Introduction

Considerable interest has been shown in determining the factors governing the mechanism and steric course of replacement reactions on cobalt(III) complexes.[1–3] Many of the reactions studied have involved complexes of the general type $[Co(en)_2XY]^{+n}$, where X, usually Cl, is the ligand replaced while Y is retained, the influence of Y on the rate, mechanism, and steric course being under investigation. Observations on the replacement of chloride and bromide ion during acid hydrolysis (aquation) and Ag^+ assisted aquation have led to the formulation of rules predicting the molecularity and possible steric course of replacement reactions.[3]

In this paper we propose to describe the configuration changes which accompany the aquation of a very labile species produced by the reaction of nitrous acid with coordinated azide ion. There is ample evidence[4,5] that free azide ion reacts with nitrous acid to form the nitrosyl azide intermediate which decomposes rapidly to yield N_2 and N_2O. If coordinated azide reacts similarly the resulting complex would be expected to be quite labile and readily aquated. Other work[6] dealing with the extent of formation of products of the type $Co^{III}(NH_3)_5L$, where the reaction of nitrous acid with the azido complex takes place in the presence of L, indicates that an intermediate species is produced initially and that water and L then compete for occupation of the sixth coordination position. We find the reaction of excess nitrous acid with either *cis*- or *trans*-$[Co(en)_2(N_3)_2]ClO_4$ in perchlorate media leads to the formation of *cis*- and *trans*-$[Co(en)_2(H_2O)_2]^{+3}$ as the only cobalt-containing products.

Experimental

Materials. ***cis*-$[Co(en)_2(N_3)_2]ClO_4$.**—The nitrate salt was prepared from cobalt(II) according to the procedure of Staples and Tobe[7] and was twice recrystallized to remove any *trans* isomer which may have been present. The perchlorate salt was obtained by adding excess sodium perchlorate to a warm solution of the nitrate salt and cooling in ice. To ensure complete conversion to the perchlorate, the above procedure was repeated twice. The salt was washed with ethanol and ether and stored in a desiccator.

Anal. Calcd. for *cis*-$[Co(en)_2(N_3)_2]ClO_4$: C, 13.25; H, 4.68; N, 38.63; Co, 16.25. Found: C, 13.52; H, 4.68; N, 38.44; Co, 16.22.

D-*cis*-$[Co(en)_2(N_3)_2]ClO_4$ was prepared according to the procedure of Staples and Tobe[7] and was repeatedly recrystallized to remove the *cis* isomer until a constant absorption spectrum was obtained.

Anal. Found: C, 13.51; H, 4.66; N, 38.33; Co, 16.31.

***cis*- and *trans*-$[Co(en)_2N_3H_2O]^{+2}$** were not isolated in solids but studied in solutions as described later.

***cis*-$[Co(en)_2(H_2O)_2]Br_3 \cdot 2H_2O$ and *trans*-$[Co(en)_2(H_2O)_2]Br_3$** were prepared by Werner's methods,[8,9] and the spectra were found to agree with those reported.[10]

All other chemicals were reagent grade and used without further purification. Sodium nitrite solutions were standardized against ceric ion.[11]

Kinetic and Isomerization Studies.—Kinetic and isomerizations studies were carried out spectrophotometrically using a two-armed mixing chamber that fitted directly into the ground joints of a 10-cm. spectrophotometer cell. The reagents were thermostated at 25.0 ± 0.1° and pipetted into the mixing chamber.

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