BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1284—1288 (1976) [Vol. 49, No. 5

Studies of the Ruthenium(III) Complexes. XII1) Kinetic Studies of the Deammonation-anation Reactions of Halogenopentaammineruthenium(III) Complexes in the Solid State

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(Received June 9, 1975)

The kinetics of the thermal substitution reaction of chloro- and bromopentaammineruthenium(III) complexes has been studied in the solid state. The reaction rates and kinetic parameters were determined for these reactions: $[RuX(NH_3)_5]Y_2(s) \rightarrow [RuXY(NH_3)_4]Y(s) + NH_3(g)$, and (X=Cl, Br: Y=Cl, Br, I, NO_3). The values of the rate constant (s^{-1}), the activation energy (kcal mol^{-1}), and the activation entropy (cal mol^{-1} K^{-1}) were 1.70×10^{-5} (at 222 °C), 41.8, and 0.7 for $[RuCl(NH_3)_5]Cl_2$; 1.02×10^{-4} (at 226 °C), 30.2, and −19.6 for $[RuCl(NH_3)_5]Br_2$; 1.35×10^{-4} (at 208 °C), 25.3, and −26.6 for $[RuCl(NH_3)_5]I_2$; 8.47×10^{-3} (at 162 °C), 29.7, and −11.5 for $[RuCl(NH_3)_5](NO_3)_2$; 1.26×10^{-4} (at 219 °C), 21.8, and −35.1 for $[RuBr(NH_3)_5]Cl_2$, and 1.17×10^{-3} (at 162 °C), 14.7, and −40.0 for $[RuBr(NH_3)_5](NO_3)_2$ respectively. The S_N1-like mechanism is favorable for the deammonation-anation reaction of all the chloropentaamine series except for the iodide, while the S_N2-like mechanism is more probable for the corresponding reaction of the bromopentaammine series. The reaction mechanism is predominantly controlled by the coordinating ability of the inner-sphere halide ion and secondarily by that of the outer-sphere anion.

The thermal decomposition of a series of halogenopentaammine halides[2,3] and nitrates[4] of cobalt(III) has been studied. The results suggest that the thermal dissociation reaction involves the following steps:

$$[CoX(NH_3)_5](NO_3)_2(s) \longrightarrow [CoX(NO_3)(NH_3)_4]NO_3(s) + NH_3(g)$$

$$[CoX(NO_3)(NH_3)_4]NO_3(s) \longrightarrow [CoX(NO_3)_2(NH_3)_3](s) + NH_3(g)$$

$$[CoX(NO_3)_2(NH_3)_3](s) \longrightarrow Co_3O_4(s) + \text{decomposition products.}$$

A recent kinetic study[5] of the thermal decomposition reaction of the series of ammine complexes of chromium(III) has reported that the thermal substitution reaction of the chloropentaamminechromium(III) chloride proceeded through the intermediate of *trans*-$[CrCl_2(NH_3)_4]Cl$.

Our own previous papers[6,7] exhibited that the thermal reactions of halogenopentaammine- *cis*-dihalogenotetraammine- and hexaammineruthenium(III) complexes were initiated by the replacement of coordinated ammonia by the outer-sphere halide ion, and the reaction mechanisms of the hexaammine- and *cis*-dihalogenotetraammineruthenium(III) complexes were proposed. In this paper, the kinetic studies of the thermal anations of $[RuX(NH_3)_5]Y_2$ (X=Cl, Br; Y=Cl, Br, I, NO_3) will be demonstrated. The influence of both inner-sphere and outer-sphere ions on the reaction mechanism will be discussed in comparison with those of the hexaammine and tetraammine series of ruthenium(III) complexes.

Experimental

Preparation of Complexes. The complexes, $[RuX(NH_3)_5]X_2$ (X=Cl, Br), were prepared by the method described in the literature.[8] $[RuCl(NH_3)_5]Y_2$ (Y=Br, I, NO_3) and $[RuBr(NH_3)_5]Y_2$ (Y=Cl, I, NO_3) were precipitated from a cold solution of ammonium halide and nitric acid.

The complexes were confirmed by elemental analysis and by visible and UV spectral measurements. $[RuCl(NH_3)_5]Cl_2$. Found: ν_{max}, 30.5×10^3 cm^{-1}; ε, 1.89×10^3 cm^{-1} M^{-1}. Ref. Value[8]: ν_{max}, $30.5 \times 10^3 cm^{-1}$; ε, 1.93×10^3 cm^{-1} M^{-1}. $[RuCl(NH_3)_5]Br_2$. Found: H, 4.05; N, 18.85%. Calcd: H, 3.96; N, 18.36%. $[RuCl(NH_3)_5]I_2$. Found: H, 3.15; N, 14.57%. Calcd: H, 3.18; N, 15.38%. $[RuCl(NH_3)_5](NO_3)_2$. Found: H, 4.67; N, 28.24%. Calcd: H, 4.37; N, 28.36%. $[RuBr(NH_3)_5]Br_2$. Found: ν_{max}, 25.1×10^3 cm^{-1}; ε, 1.93×10^3 cm^{-1} M^{-1}. Ref. Value[8]: ν_{max}, 25.1×10^3 cm^{-1}; ε, 1.92×10^3 cm^{-1} M^{-1}. $[RuBr(NH_3)_5]Cl_2$. Found: H, 4.15; N, 21.21%. Calcd: H, 4.49; N, 20.78%. $[RuBr(NH_3)_5]I_2$ Found: H, 3.03; N, 13.89%. Calcd: H, 2.91; N, 13.47%. $[RuBr(NH_3)_5](NO_3)_2 \cdot 1/2H_2O$. Found: H, 4.05; N, 25.39%. Calcd: H, 3.88; N, 25.13%.

Differential Thermal Analysis, Thermogravimetry and Isothermal Kinetic Measurement. The differential thermal analysis (DTA) and the thermogravimetry (TG) of the complexes were carried out using a Shimadzu DTG 20-type micro-differential thermobalance. All the experiments were made in a constant helium stream at a heating rate of 5 °C/min., using about a 10 mg sample in each run. In the isothermal kinetic measurement, the temperature was rapidly elevated so as to depress the decomposition of the sample before measurement and was then kept constant within ±0.5 °C. The kinetic plots were made based on mass-loss measurements at several temperatures.

A Shimadzu UV-200 recording spectrophotometer and a JASCO Model DS-403G Grating Infrared spectrophotometer were used for the measurement of the absorption spectra of the initial compounds and the reaction products.

Results and Discussion

DTA and TG Studies. The DTA and TG curves of the chloropentaammineruthenium(III) bromide and iodide, and the bromopentaammineruthenium(III) chloride and iodide are given together in Fig. 1, while those of the nitrates are given in Fig. 2.

The DTA curves are characterized by endothermic peaks for the chloropentaammine series at 327 °C (bromide) and 291 °C (iodide). Shoulders were found, however, corresponding to the mass-loss of one or two

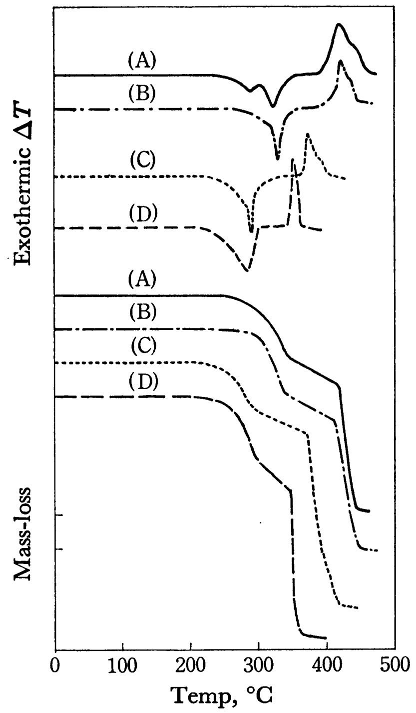

Fig. 1. DTA and TG curves of the halogenopentaammineruthenium(III) halides.
$[RuCl(NH_3)_5]Y_2$; bromide (B), iodide (C).
$[RuBr(NH_3)_5]Y_2$; chloride (A), iodide (D).

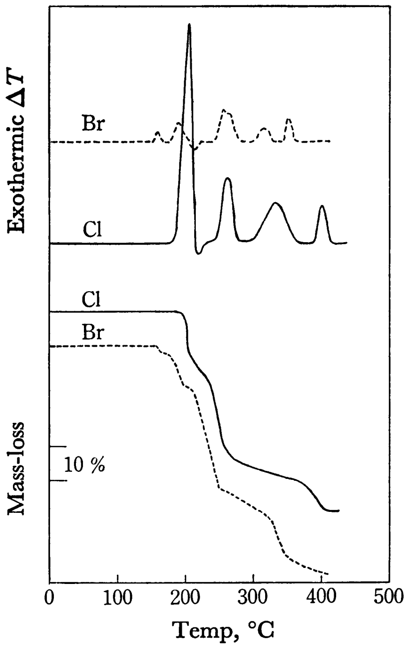

Fig. 2. DTA and TG curves of the halogenopentaammineruthenium(III) nitrate.
$[RuX(NH_3)_5](NO_3)_2$; (X=Cl, Br).

moles of ammonia at 310 °C and 285 °C respectively. For the bromopentaammine chloride, a small endothermic peak at 288 °C was clearly found, besides a large broad endothermic peak at 320 °C, and a broad endothermic peak was found at 284 °C for the bromopentaammine iodide. On the other hand, the DTA curves of the nitrates for both series are characterized by several exothermic peaks, different from those of the halides. For the bromopentaammine nitrate, the first exothermic peak at 158 °C was found, by the elemental analysis and the mass-loss measurement, to be corresponding to the liberation of $1/2 \cdot H_2O$. This may be attributable to the physico-chemical rearrangements of the crystalline lattice or the coordination structure after the coordinated water liberation. However, a detailed interpretation must await further investigations.

The initial temperature of mass-loss for the deammonation is as follows: $[RuBr(NH_3)_5](NO_3)_2$ (176 °C), $[RuCl(NH_3)_5](NO_3)_2$ (190 °C), $[RuCl(NH_3)_5]I_2$ (215 °C), $[RuBr(NH_3)_5]I_2$ (239 °C), $[RuCl(NH_3)_5]Br_2$ (243 °C), $[RuBr(NH_3)_5]Br_2$ (244 °C), $[RuCl(NH_3)_5]Cl_2$ (246 °C), $[RuBr(NH_3)_5]Cl_2$ (247 °C).

The main decomposition reaction, probably taking place during the first endo- or exothermic reaction, might be accompanied by the continuous evolution of such gases as ammonia, free halogen, or ammonium halide, as reported in a previous paper⁶⁾ on the halogenopentaammine halides. On the other hand, for the nitrates, only the ammonia gas was identified in the initial period of the thermal decomposition; the analyses of such gases as NO, N_2O, N_2 and H_2O which were identified in the thermal decomposition of halogenopentaamminecobalt(III) nitrate⁴⁾ have not yet been successful.

As a result, there were not so many differences among the thermal decomposition reactions of the halogenopentaammine series of complexes, except for those of the nitrates. However, the nitrates and the iodides all seem to be thermally unstable.

Stoichiometry and Kinetic Study. It has already been reported⁶⁾ that the thermal decomposition reactions of chloropentaammine chloride (at 246—396 °C) and bromopentaammine bromide (at 244—398 °C) can be expressed by Eq. 1:

$$[RuX(NH_3)_5]X_2 \longrightarrow [RuX_3(NH_3)_3] + 2NH_3 \quad (X=Cl, Br) \qquad (1)$$

In the present isothermal experiment it was found that the reaction actually proceeded *via* successive steps which were composed of unimolecular deammonations, because the isothermal decomposition products of the initial complex were each composed of one mole of ammonia and dihalogenotetraammine halides or nitrate. All the solid reaction products were identified by elemental analysis or absorption spectrophotometry; the results are listed in Tables 1 and 2. The results for the elemental analysis of a reaction product are not necessarily in agreement with the calculated value for chemical formulas corresponding to the liberation of one molar ammonia, except for the chlorobromotetraammine bromide. This might be attributed to the instability of the reaction product at the decomposition temperature or to the low reproducibility in this sort of thermal decomposition reaction. Unfortunately, the configurations of tetraammine complexes can not be clearly determined from the absorption spectra, especially for the mixed halide-ligand complexes. In the IR spectra of $[RuCl(NH_3)_5](NO_3)_2$ and its reaction

Table 1. Analysis of the reaction product of chloropentaammineruthenium(III)

Initial complex	Chloride	Bromide	Iodide	Nitrate
Sample color	dark green	dark yellow	black	brown
Chemical formula assigned	$[RuCl_2(NH_3)_4]Cl$	$[RuClBr(NH_3)_4]Br$	$[RuClI(NH_3)_4]I$	$[RuCl(NO_3)(NH_3)_4](NO_3)$
Elemental analysis found (H%, N%)	(4.82, 21.10)	(3.31, 15.50)	(2.18, 11.28)	(3.89, 27.14)
calcd	(4.40, 20.38)	(3.32, 15.38)	(2.64, 12.22)	(3.68, 25.57)
Electronic spectrum (ν_{max}, $10^3 cm^{-1}$, ε; $10^3 M^{-1} cm^{-1}$)	(30.6, 1.70) (35.7, 2.19)	(30.6, 0.93) (25.6, 1.10)	(30.6, 0.65) (18.3, 1.24)	(30.6, 1.60)
Initial spectrum	(30.5, 1.89) (30.5, 1.93)[a]	(30.6, 1.56)	(30.6, 1.92)	(30.6, 1.89)

a) Published value from Ref. 8.

Table 2. Analysis of the reaction product of bromopentaammineruthenium(III)

Initial complex	Chloride	Bromide	Iodide	Nitrate
Sample color	brown	brown	black	yellow
Chemical formula assigned	$[RuClBr(NH_3)_4]Cl$	$[RuBr_2(NH_3)_4]Br$	$[RuBrI(NH_3)_4]I$	$[RuBr(NO_3)(NH_3)_4](NO_3)$
Elemental analysis found (H%, N%)	(4.13, 17.23)	(3.61, 14.46)	(2.67, 11.80)	(3.38, 23.57)
calcd.	(3.78, 17.51)	(2.96, 13.70)	(2.41, 11.14)	(3.25, 22.53)
Electronic spectrum (ν_{max}, $10^3 cm^{-1}$, ε; $10^3 M^{-1} cm^{-1}$)	(25.1, 1.14) (30.5, 1.41)	(25.2, 1.12) (30.3, 1.83)	(18.3, 2.10) (25.6, 1.06)	(25.2, ——)
Initial spectrum	(25.2, 1.72)	(2.51, 1.95) (2.51, 1.92)[a]	(25.2, 2.20)	(25.2, 1.40)

a) Published value from Ref. 8.

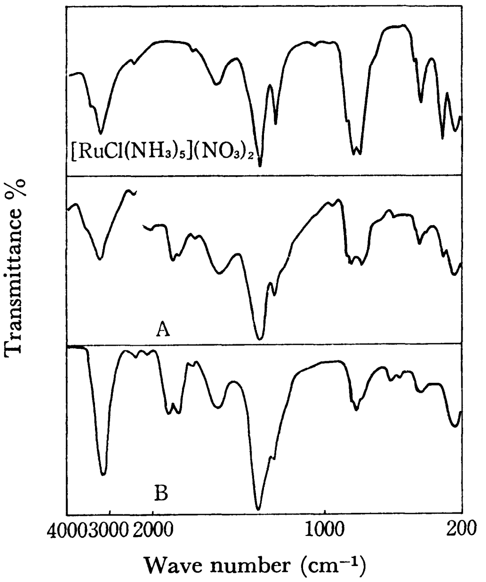

Fig. 3. IR spectra of initial complex and thermal decomposition products.
Chemical formura assigned
A: $[RuCl(NO_3)(NH_3)_4](NO_3)$
B: $[RuBr(NO_3)(NH_3)_4](NO_3)$

products, shown in Fig. 3, new absorption bands were found at 1850—1900 cm^{-1} and 570—600 cm^{-1}; the former was assigned to the ν(NO) of the coordinated NO_3^- and the latter, to the ν(Ru–NO_3) or ν(Ru–ONO_2).[9,10]

Thus, the thermal decomposition reaction can be expressed by Eqs. 2 and 3:

$$[RuCl(NH_3)_5]X_2 \longrightarrow [RuClX(NH_3)_4]X + NH_3 \quad (X=Br, I, NO_3) \qquad (2)$$

$$[RuBr(NH_3)_5]X_2 \longrightarrow [RuBrX(NH_3)_4]X + NH_3 \quad (X=Cl, I, NO_3) \qquad (3)$$

In the isothermal kinetic measurements, the ranges of temperature applied were decided with reference to the results of DTA and TG studies. Plots of $\ln\{a/(a-x)\}$ *vs.* the reaction time for Reactions 2 and 3 obtained from the isothermal measurements are illustrated in Figs. 4 and 5, where a is the initial mass of the sample, and $a-x$ the mass at the reaction time t. The plots give a straight line with a good reproducibility in each measurement. A similar relationship was obtained for the other complexes. As a result the thermal decomposition can be regarded as a first-order reaction with respect to the reactant. The Arrhenius plots for the reactions are given in Fig. 6, while the rate constants obtained from the slope of the straight line are listed in

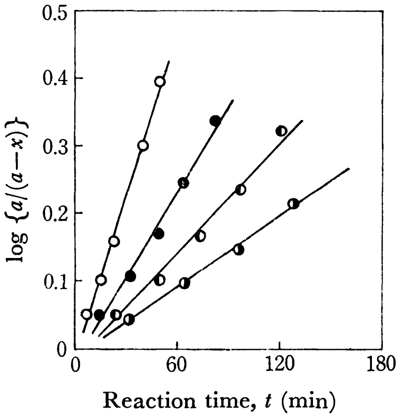

Fig. 4. Plots of a first-order rate equation for the deammonation-anation reaction of $[RuCl(NH_3)_5]Br_2$.
○ 243 °C, ● 237 °C, ◐ 226 °C, ◑ 219 °C

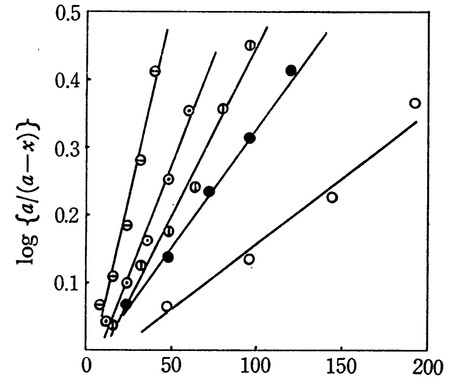

Fig. 5. Plots of a first-order rate equation for the deammonation-anation reaction of $[RuCl(NH_3)_5](NO_3)_2$. ⊖ 168 °C, ⊙ 166 °C, ⦶ 162 °C, ● 154 °C, ○ 151 °C

Table 3. Kinetic parameters for the deammonation-anation reaction of Ru(III) and Cr(III) compounds

Compound	$k\times10^5\,s^{-1}$ (177 °C)	E_a (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	log A
$[Ru(NH_3)_6]Br_3$	5.05	23.3	−29.3	7.0
$[Ru(NH_3)_6]I_3$	27.1	20.7	−31.6	6.5
$[RuCl(NH_3)_5]Cl_2$	0.02	41.8	0.7	13.6
$[RuCl(NH_3)_5]Br_2$	0.36	30.2	−19.6	9.2
$[RuCl(NH_3)_5]I_2$	1.96	25.3	−26.8	7.6
$[RuCl(NH_3)_5](NO_3)_2$	29.2	29.7	−11.5	13.1
$[RuBr(NH_3)_5]Cl_2$	1.44	21.8	−35.1	5.8
$[RuBr(NH_3)_5]Br_2$	0.42	26.1	−34.3	7.5
$[RuBr(NH_3)_5]I_2$	10.34	15.6	−44.9	3.6
$[RuBr(NH_3)_5](NO_3)_2$	314	14.7	−40.0	4.6
cis-$[RuCl_2(NH_3)_4]Cl$	6.75	33.1	−6.9	11.9
cis-$[RuBr_2(NH_3)_4]Br$	10.0	31.3	−10.1	11.2
$[Cr(NH_3)_6]Cl_3$	4.0(174)	30	−12	a)
$[CrCl(NH_3)_5]Cl_2$	2.8(198)	39	1.4	
cis-$[CrCl_2(NH_3)_4]Cl$	16 (142)	31	−2.3	

a) From Ref. 5.

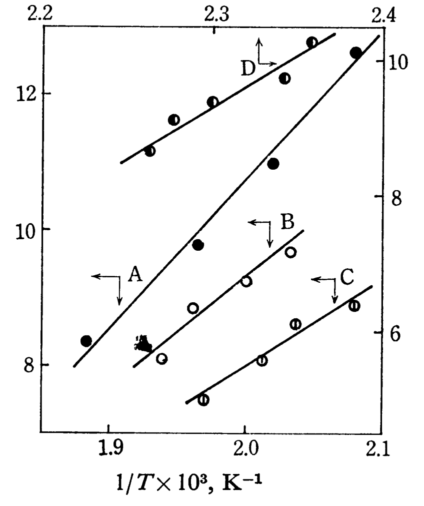

Fig. 6. Arrhenius plots of the substitution reaction for chloropentaammineruthenium(III).
$[RuCl(NH_3)_5]Y_2$; chloride (A), bromide (B), iodide (C), nitrate (D).

Table 3, together with the kinetic parameters.

It can be seen that, in general, the rate constants for the deammonation reactions of the chloropentaammine series are smaller than those of the bromopentaammine series. In both cases, the influence of the outer-sphere anion species on the reaction rate is to enhance it in the following order; $Cl<Br<I<NO_3$.

By a comparison with the other ammine complexes, it was found that the rate constants decrease in the order of tetraammine>hexaammine>pentaammine, as has also been seen for the chromium(III) chloride complexes (Table 3). However, the activation energies do not necessarily decrease with the increase in rate constants. Moreover, the values of the activation entropy are smaller in this order: tetraammine>pentaammine≈hexaammine. These facts suggest that the reaction mechanisms for the deammonation and the anation of the outer-sphere anion are different from each other among the reactions of the three series of ammine complexes. It may be considered that the coordinated halide ligand is also one of the determinants on the reaction mechanism.

Reaction Mechanism of the Deammonation-anation. In a previous paper,[7] we discussed how the mechanism seems to belong to the S_N2 category for the substitution reaction of the hexaammine series of complexes, while the S_N1 mechanism is favorable for that of the tetraammine series, considering the values of the kinetic parameters and the contribution of the π-bonding nature between the metal and the ligand.

The reaction rates of the chloropentaammine series of complexes are smaller than those of the corresponding bromopentaammine series, and the former reveal large values of the activation energy. Yet the values of the activation entropy of the former (0—-20 cal·mol^{-1}·K^{-1}) are larger than those of the latter (-34—-45 cal·mol^{-1}·K^{-1}). Therefore, for the substitution reaction of the chloropentaammine series of complexes, the S_N1-like mechanism may be favorable.

The activation energies of deammonation-anation reactions should be rather close to each other, but there are some differences among the values of the activation energies for the reactions of complexes with different outer-sphere anions. This suggests that the substitution reaction mechanism is affected by the nucleophilic characters of the coordinated ligand and the outer-sphere anion. That is to say, in the chloropentaammineruthenium(III) iodide and nitrate, the deammonation-anation reaction may proceed *via* the S_N1-like (partially the S_N2-like) mechanism. On the other hand, considering the small values of the activation energy (15—26 kcal·mol^{-1}) and the large negative values of the activation entropy (-34—-45 cal·mol^{-1}·K^{-1}), the mechanism for the reaction of the bromopentaammine series seems to belong to the S_N2 category.

Reviewing the thermal substitution reactions of the hexaammine-, pentaammine-, and tetraammineruthenium(III) complexes, the rate constants increase in the following order of the outer-sphere anion: $Cl<Br<I<NO_3$. That the nitrates gave the largest value of the rate constants may be attributable to the nucleophilic character, as has also been in the kinetic study[11] of the

deaquation-anation reaction of the aquapentaammineruthenium(III) series. The iodides also gave larger values of the rate constants than those for the other halide ions. This might be attributed to the back-donation of π-electrons from the 4d-orbital electron of the ruthenium(III) ion to the vacant d orbitals of the iodide ion, for the outer-sphere anion might be fixed by the lattice energy.

The reaction mechanisms thus determined can be classified by the order of the frequency factor as is shown in Table 3. The order of the frequency factor, A, is $10^3\,s^{-1}$—$10^7\,s^{-1}$ for the S_N2 mechanism, while that for the S_N1 mechanism ranges from $10^9\,s^{-1}$ to $10^{13}\,s^{-1}$. A reasonable discussion of this classification can now be undertaken.

The authors wish to thank the Ministry of Education for the financial support (No. 847009) granted to this research.

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