TABLE V

TYPICAL DATA FOR THE EVALUATION OF THE EQUILIBRIUM CONSTANT K[a]

$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{obsd}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{S}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH(area)}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}^{b}$	$\left(\frac{C_4H_8}{C_4H_{10}}\right)_{RH}[RH]$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}\frac{[Cu(OAc)_2]}{[RH]}$
0.83	0.14	0.69	0.58	1.7	1.6×10^{-3}
0.95	0.16	0.79	0.66	1.5	1.4×10^{-3}
1.5	0.28	1.2	1.0	0.97	1.1×10^{-3}
2.3	0.50	1.8	1.5	0.64	0.81×10^{-3}

[a] RH = n-butyraldehyde (0.966 M); solvent: glacial acetic acid. [b] $(C_4H_{10}/C_4H_8)_{area} = 1.2 \times (C_4H_{10}/C_4H_8)_{molar}$.

According to eq. 18 and 19, the ratio of butane to butene in the blank divided by that in the presence of hydrogen donor should be related to the solvent and hydrogen-donor concentrations as in eq. 17. At constant substrate and varying cupric acetate concentration, the right-hand side of eq. 20 should be

$$\left[\frac{C_4H_{10}}{C_4H_8}\right]\left[\frac{C_4H_8}{C_4H_{10}}\right]_{RH} = \frac{k_s[HOAc]}{k_e[RH]} \qquad (20)$$

constant, if the treatment is valid. This check is established in Table VI for a typical example.

TABLE VI

ALKANE/ALKENE FROM THE BLANK AS CORRECTION[a]

Cupric acetate, M	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_S$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}$	$\left(\frac{C_4H_{10}}{C_4H_8}\right)_S \Big/ \left(\frac{C_4H_{10}}{C_4H_8}\right)_{RH}$
2.60×10^{-3}	0.012	0.24	0.050
6.50×10^{-4}	0.044	0.89	0.050
3.90×10^{-4}	0.066	1.4	0.047
2.60×10^{-4}	0.10	2.0	0.050

[a] RH = n-butyraldehyde (2.58 M) in 64 mole % aqueous acetic acid.

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The Reaction of Vanadium(IV) and Chromium(II) Ions in Acid Solution. Kinetics and Mechanism of Decomposition of a Dinuclear Cr(III)–V(III) Intermediate[1]

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A study has been made of the kinetics of the reaction of vanadium(IV) and chromium(II) in acidic perchlorate solutions. Rate measurements at low $[H^+]$ establish that the major fraction of the reaction occurs quite rapidly; a small portion of the reaction proceeds by way of a dinuclear intermediate, $VO(OH)_nCr^{4-n}$. The direct reaction and the intermediate formation occur rapidly ($k > 8 \times 10^3\ M^{-1}\ sec.^{-1}$ at 5.0°). The intermediate decomposes to $V^{3+} + Cr^{3+}$ at a measurable rate obeying pseudo-first-order kinetics. The rate exhibits a complex dependence upon hydrogen ion concentration (0.01–1 F $HClO_4$ at 1.00 M ionic strength). A mechanism is proposed involving an acid ionization equilibrium which can be verified independently from spectral studies on the intermediate. The equilibrium quotient and decomposition rates were measured at 5–25° and the corresponding thermodynamic activation parameters were evaluated. The rate of this decomposition reaction is compared with that in several related systems, and a general correlation found of decomposition rate and substitution lability of the metal ion involved.

Introduction

During a previous study[2] of the kinetics of reaction of vanadium(III) and chromium(II) ions, kinetic evidence was found for the existence of steady-state concentrations of an unstable reaction intermediate, $V(OH)_nCr^{4-n}$,[3] formally a V(III)–Cr(II) or V(II)–Cr(III) species. This paper describes a study of the formation and decomposition of a previously unknown V(III)–Cr(III) dimeric species.

A Cr(III)–Cr(III) binuclear ion, $CrOCr^{4+}$, the major Cr(III)-containing product of reaction of Cr(IV) (presumably) and Cr(II),[4] is a solution species with reasonably well-understood structure and reaction properties.[5,6] A dimer of vanadium(III), VOV^{4+}, is an intermediate present at low concentration during reaction of V(IV) and V(II).[7] A dimer of Fe(III) is

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[1] This work was performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Presented before the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[2] J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

[3] The extent of proton association and the degree of hydration and the matter of oxo or hydroxo bridging remains unresolved by these experiments.

[4] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[5] (a) R. E. Connick and Sr. M. G. Thompson, 148th National Meeting of the American Chemical Society, Inorganic Division, Papers 23, 24, Sept. 1964; (b) Sr. M. G. Thompson, Thesis, University of California, Berkeley, 1964, UCRL 11410; (c) R. W. Kolaczkowski and R. A. Plane, *Inorg. Chem.*, **3**, 322 (1964).

[6] In many instances it is convenient to write the "simplest" formula for these dimeric ions, even in the case of the chromium(III) dimer, for which the formula is $[Cr(OH_2)_4OH]_2^{4+}$ (ref. 5). In addition, there are at least two other dimeric chromium(III) species which can reach equilibrium with this ion; the species $CrOHCr^{5+}$ and/or $CrOHCrOH^{4+}$ are the ones which decompose directly to monomeric Cr(III) (ref. 5b).

[7] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964).

known,[8] and more recently it has been reported[9] to be the preliminary product in the reaction of Fe(II) with some 2-equiv. oxidizing agents; it presumably arises from reaction of Fe(II) and Fe(IV). In acid solution these dimeric ions dissociate spontaneously to the aquo ions Cr^{3+}, V^{3+}, and Fe^{3+}, respectively.

In view of the mode of formation of these ions, attempts were made to prepare a V(III)–Cr(III) dimer as an intermediate in the reaction of V(IV) and Cr(II). On mixing the ions V(IV) and Cr(II), each of which is a pale blue color, a bright green color develops instantly; this color slowly fades to the blue-purple color characteristic of the aquo ions of V(III) and Cr(III) in perchloric acid solution. This paper reports on the dimeric ion, its formation, spectrum, acid dissociation, and especially the kinetics and mechanism of its subsequent decomposition. An earlier brief report of the phenomenon of intermediate formation in the V(IV)–Cr(II) reaction has been published.[10]

Experimental

Reagents.—Two independent sources of every reagent except perchloric acid were employed. Vanadium(IV) perchlorate solutions were prepared from reagent grade vanadyl sulfate and recrystallized barium perchlorate and from electrolytic reduction of specially purified vanadium pentoxide. Chromium(II) perchlorate solutions were prepared by electrolytic reduction of purified chromium(III) perchlorate solutions and from dissolution of high-purity electrolytic chromium metal[11] in dilute perchloric acid. These preparations and the analyses of the solutions have been described previously.[2,12] Lithium perchlorate, used to maintain constant ionic strength, was the commercial reagent grade compound or was prepared from lithium carbonate and perchloric acid; in both cases the solid was recrystallized twice before use. Perchloric acid (Baker, 72% reagent grade) was used without purification. Water used in preparations and reaction solutions was a double distillation of laboratory distilled water from alkaline permanganate in a tin-lined Barnstead still.

Kinetic Experiments.—Solutions complete but for chromium(II) were mixed in 5-cm. spectrophotometer cells and sealed with a rubber serum cap. The solution and cell were purged of dissolved oxygen by flushing for at least 15 min. with a stream of nitrogen purified by successive passage through two chromium(II) solutions, dilute sodium hydroxide, and water. The cells were placed in a small constant temperature water bath positioned in the light beam of a Cary Model 14 recording spectrophotometer. (Details of this thermostating arrangement have been published previously.[12]) The reaction was started with injection of the appropriate volume of chromium(II) stock solution with a calibrated syringe and needle. The contents were then rapidly mixed, and a recording was made of absorbance as a function of time. The synchronized motor of the spectrophotometer chart drive served as timer for the absorbance readings. An electric timer was started by a foot switch at the instant the chromium(II) was introduced. The delay between true zero time and the first recorded reading usually amounted to 4–7 sec. and could be read for each run from the timer. Absorbance readings were generally taken over at least 95% reaction.

The reaction rate was measured over a range of wave lengths, from 2600 to 7600 Å. In every instance the absorbance readings during a run were substantially higher than consistent with contributions from only the reactants and eventual products.

Kinetic Data.—The decay of the absorbance to its equilibrium value in each run follows a first-order rate equation. The apparent first-order rate constant in each run was evaluated from 7–20 absorbance readings, usually extending over at least 90% reaction, using the least-squares computer program described previously.[2] No systematic deviations of observed and calculated absorbance were noted, and the rate constants are independent of wave length. Over the range of acid concentrations and temperatures studied, the half-times ranged from 2.5 to 136 sec.

A number of duplicate runs were performed using the alternate preparations of reagents. These solutions led to identical kinetic behavior in every instance, indicating the probable absence of catalytically effective impurities.

Reaction Stoichiometry.—In perchloric acid solution, the calculated equilibrium quotient is $\sim 10^{13}$ for the reaction

$$VO^{2+} + Cr^{2+} + 2H^+ = V^{3+} + Cr^{3+} + H_2O \qquad (1)$$

The subsequent reduction of V^{3+} by Cr^{2+} is also favorable,[2] with an equilibrium quotient of $\sim 10^3$; no complications arose from simultaneous occurrence of this reaction, however, since concentrations in these experiments were selected with Cr^{2+} completely oxidized by V(IV), leaving no Cr^{2+} to reduce V^{3+}. In addition, V^{3+} is stable to disproportionation. The equilibrium absorbance values in each run are consistent with the stoichiometry indicated in eq. 1. In each experiment the final reading was within experimental error of the value calculated from the independently known molar absorbancy indices and the concentrations calculated on the basis that reaction 1 occurred essentially to completion as written.

Results

Formation of the Intermediate.—Even in the experiments at the lowest reactant concentrations and at 5.0°, there was no spectral evidence of any delay in disappearance of the reactants or in formation of the reaction intermediate. The time lapse between mixing and the first point was generally ~5 sec., and at least 95% reaction, a conservative estimate, had occurred in this interval. The solution initially 4.8×10^{-4} *F* in each metal ion reactant would provide the lowest rate of formation of intermediate. With the assumption that the rate equation has the form $k_i[VO^{2+}][Cr^{2+}]$, these estimates establish $k_i \geq 8 \times 10^3 M^{-1}$ sec.$^{-1}$ at 5.0°.

Since the intermediate forms at a rate exceeding the limit of this technique, it has not been possible to measure directly the extent to which the reaction proceeds along the path involving this intermediate (as opposed to a "direct" reaction rapidly forming V^{3+} and Cr^{3+}). It has proved possible, however, to study this problem indirectly, by making use of the dependence of the reaction rate upon $[H^+]$, in runs where $[H^+]$ changes appreciably during the reaction.[13] To discuss the consequences of appreciable changes in $[H^+]$, one must anticipate the rate law for decomposition of the intermediate and its dependence upon $[H^+]$. The exact equations will be presented in a subsequent section, but we may note here that the reaction obeys first-order kinetics with respect to the intermediate and that the

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[8] R. M. Milburn and W. C. Vosburgh, *J. Am. Chem. Soc.*, **77**, 1352 (1955); R. M. Milburn, *ibid.*, **79**, 537 (1957).

[9] T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *ibid.*, **87**, 926 (1965).

[10] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).

[11] *The author is grateful to Prof. J. P. Fackler for suggesting this* method of preparation of Cr(II) solutions. The chromium was purchased from United Mineral and Chemical Corp., New York, N. Y.

[12] J. H. Espenson, *J. Am. Chem. Soc.*, **86**, 5101 (1964).

[13] The author is grateful to a referee for suggesting this type of experiment.

TABLE I

VARIATIONS IN HYDROGEN ION CONCENTRATION

Conditions: 15.0°, ionic strength 1.00 M ($LiClO_4$), 5.00-cm. optical path

$[VO^{2+}]_0$, M	$[Cr^{2+}]_0$, M	$[H^+]_0$, M	$[H^+]_{eq}$, M	k, sec.$^{-1}$
Group 1. Approximately Constant $[H^+]$				
0.00051	0.000485	0.0110	0.0100	0.0130
0.00102	0.00097	0.0120	0.0100	0.0124
0.00051	0.000485	0.0150	0.0140	0.0138
0.00051	0.000485	0.0200	0.0190	0.0159
0.00051	0.000485	0.0300	0.0290	0.0190
Group 2. Varying $[H^+]$				
0.0102	0.00985	0.032	0.012	0.0135, 0.0137
0.0051	0.00492	0.021	0.011	0.0130

order with respect to $[H^+]$ is *ca.* 0.4 from 0.01 to 0.03 M H^+.

We may consider two limiting cases: (a) the reaction proceeds almost entirely by way of the intermediate, and (b) the path involving the intermediate accounts for only a very small fraction of the reaction, most of which involves "direct" formation of the products. In case (a), $[H^+]$ falls steadily from its initial value to $C_0 - 2[Cr^{2+}]_0$ at completion, whereas in case (b), $[H^+]$ remains essentially constant at $C_0 - 2[Cr^{2+}]_0$ during the course of the run. The value of the pseudo-first-order rate constant and the dependence of rate upon $[H^+]$ should distinguish these limiting cases. Experiments were performed at low $[H^+]$ (0.01–0.03 M) with $[VO^{2+}]_0$ and $[Cr^{2+}]_0$ quite low ($\sim 5 \times 10^{-4}$ M) to minimize any change in $[H^+]$ due to reaction. Experiments were also performed under similar conditions, except that $[VO^{2+}]$ and $[Cr^{2+}]$ were larger and $[H^+]$ decreased substantially. These data, summarized in Table I, establish that the specific rate of decomposition of the intermediate remains constant throughout each experiment and that it is the value of $[H^+]$ *at completion* which fixes its value. This situation is apparently that in case b: only a small fraction of reaction proceeds through the intermediate, with the major portion (>90%) of the products formed in a more rapid reaction. That the absorbance changes due to the decomposition reaction are so large at some wave lengths implies intense light absorption of the intermediate rather than a significant concentration.

These results do not imply that the mechanism of the direct reaction path which carries the bulk of the reaction is necessarily simple, but only that its rate lies beyond these experiments. It is noteworthy, also, that the direct reaction apparently does not involve a 2-equiv. change with Cr(IV) and V(II) as intermediates, for the dominant chromium(III) product is Cr^{3+} and not dimeric Cr(III), which would result from reaction of Cr(IV) and Cr(II)[4]; furthermore, there is no spectral evidence at 4250 Å. for VOV^{4+}, which would be formed were V(II) generated in the presence of V(IV).[7]

Decomposition of the Intermediate.—Rate measurements were carried out with initial concentrations of V(IV) and Cr(II) varied from 4×10^{-4} to 1.1×10^{-2} F.

TABLE II

DEPENDENCE OF INTERMEDIATE DECOMPOSITION RATE AND LIGHT ABSORPTION ON REACTANT CONCENTRATIONS

Conditions: 25.0°, 0.200 F $HClO_4$, $I = 1.00$ M ($LiClO_4$), 3000 Å., $b = 5.00$ cm.

$[VO^{2+}]_0$, M	$[Cr^{2+}]_0$, M	$t_{1/2}$, sec.	ΔA	$\Delta A/b[Cr^{2+}]_0$, M^{-1} cm.$^{-1}$
0.00546	0.00070	4.51	0.537	153
0.00164	0.00142	4.57	1.16	164
0.00280	0.00147	4.83	0.04	141
0.00560	0.00147	4.65	1.06	144
0.0112	0.00144	4.65	1.03	143
0.00285	0.00285	4.45	2.40	168
0.00546	0.00292	4.68	2.26	155
0.0112	0.00292	4.71	2.19	150
0.00546	0.00539	4.65	4.20[a]	156
0.0112	0.00584	4.59	4.42[a]	151
0.0112	0.0109	4.34	8.96[a]	164

[a] The extrapolation of $A - A_\infty$ to the time of mixing involved somewhat longer time intervals in runs where the initial absorbance was substantially larger than 2; in the last run the interval was 9.9 sec., and in the next to last, 7.8 sec.

(In every experiment, $[Cr(II)] \leq [V(IV)]$, to avoid reduction of V(III) by Cr(II), a process which occurs at a rate not substantially lower than those involved here.[2]) The decomposition of the reaction intermediate follows pseudo-first-order kinetics, and the rate constants show no specific trends with V(IV) or Cr(II) concentrations in the ranges studied. Table II summarizes the results of a typical series of experiments, at 25.0°, 0.200 F $HClO_4$, and ionic strength 1.00 M ($LiClO_4$). These data also provide information on the reproducibility of the rate measurements, which was generally 2–3%.

Hydrogen ion, however, exerts a specific rate effect. Table III summarizes the values of k obtained on variation in acidity from 0.010 to 0.99 F $HClO_4$, at 5.0, 15.0, and 25.0°. The average rate constants in this table represent values from at least two runs, and in computing these averages the individual rate constant in each run was weighted by 1/variance of the fit of observed and calculated absorbance readings. The general rate behavior is an increase of rate with increasing $[H^+]$, but the detailed behavior is more complicated. Interpretation of these data in terms of an empirical rate equation is best done by examining the slopes of a plot of log k *vs.* log $[H^+]$, Figure 1. At both extremes of acid concentration, the dependence of reaction rate upon $[H^+]$ is less than at intermediate $[H^+]$, where the slope of such a plot is as large as 0.7. This rate behavior suggests an acid ionization equilibrium and a rate equation of the form

$$k = (AQ + B[H^+])/(Q + [H^+]) \qquad (2)$$

in which A and B represent empirical rate parameters and Q represents an equilibrium quotient for an acid ionization reaction. The data (k, $[H^+]$, T) were fitted to this empirical relation by a computer. The temperature dependence of the parameters A and B was assumed to follow the Eyring absolute rate theory equation; the temperature dependence of Q was assumed to

TABLE III

APPARENT FIRST-ORDER RATE CONSTANTS (SEC.$^{-1}$) AT VARIOUS $HClO_4$ CONCENTRATIONS AND TEMPERATURES

	5.0°		15.0°		25.0°	
$HClO_4$, *F*	Obsd. (no expts.)	Calcd.[a]	Obsd. (no expts.)	Calcd.[a]	Obsd. (no expts.)	Calcd.[a]
0.0100	0.00532 (2)	0.00538	0.0130 (2)	0.0121		
0.0300	0.0099 (2)	0.0101	0.0203 (2)	0.0210	0.0423 (2)	0.0422
0.0500					0.0559 (4)	0.0575
0.0600	0.0158 (2)	0.0165	0.0330 (2)	0.0334	0.0626 (2)	0.0648
0.100	0.0239 (2)	0.0238	0.0498 (2)	0.0481	0.0920 (4)	0.0924
0.139	0.0307 (2)	0.0299	0.0635 (2)	0.0608		
0.200	0.0386 (2)	0.0379	0.0804 (7)	0.0780	0.151 (18)	0.151
0.320			0.1095 (5)	0.1049	0.203 (3)	0.207
0.500	0.0592 (2)	0.0615	0.134 (2)	0.134	0.273 (3)	0.270
0.750	0.0735 (2)	0.0718	0.158 (4)	0.160		
0.990	0.0770 (2)	0.0782	0.179 (4)	0.178		

[a] From the activation parameters in Table IV and eq. 2.

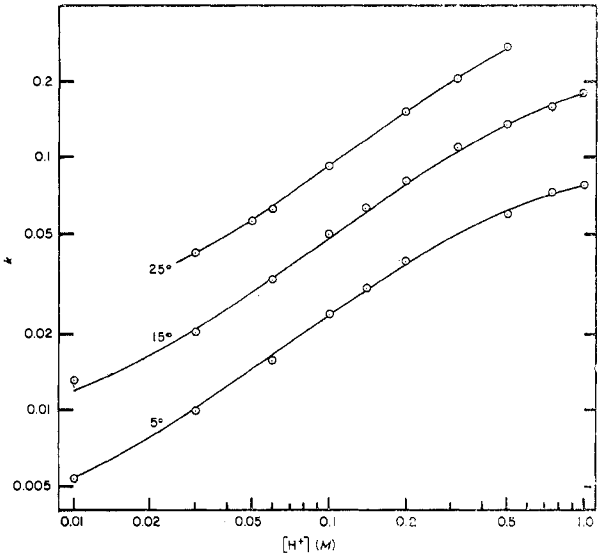

Figure 1.—Logarithmic plots of *k* vs. [H$^+$] illustrating the apparent order with respect to [H$^+$] and conformity of the data to eq. 2. The curves shown are those calculated from the values of ΔH^* and ΔS^* in Table IV.

TABLE IV

SUMMARY OF HYDROGEN ION AND TEMPERATURE DEPENDENCES

Parameter[a]	ΔH^*, kcal. mole^{-1}	ΔS^*, cal. mole^{-1} deg.$^{-1}$	Value at 25.0°
$A(k_0)$	14.6 ± 0.8	-17.6 ± 2.6	0.0170 sec.$^{-1}$
$B(k_1)$	14.0 ± 0.2	-12.3 ± 0.7	0.645 sec.$^{-1}$
Q[b]	4.93	16.0	0.739 *M*

[a] With the empirical parameters *A* and *B* identified as referring to the reaction steps in eq. 4 and 5. [b] $Q = \exp(16.0/R) \exp(-4930/RT)$. [c] Uncertainties represent standard deviations; they were calculated assuming $Q(T)$ is without uncertainty and represent lower limits.

be of the form $Q = e^{\Delta S°/R}e^{-\Delta H°/RT}$. The rate constants, averaged as described previously, were weighted as $1/k^2$, and the computation sought the best values of the parameters to fit the average *k* values at all hydrogen ion concentrations and temperatures simultaneously. This computation was performed by estimating values of $Q(T)$ and then allowing the computer program to calculate *A* and *B* and their activation parameters. This computation was repeated, seeking values of *Q* with the appropriate temperature dependence, which resulted in the best set of values for the rate parameters. Table IV summarizes the results of this computation. The parameters tabulated here calculate specific rates with a r.m.s. deviation of 2.8%. The comparison of observed and calculated values is made in Table III.

The rate data establish that a small fraction of the reaction of V(IV) and Cr(II) involves an intensely colored intermediate which undergoes subsequent decomposition to V^{3+} and Cr^{3+}. These data do not reveal, however, the formula of the intermediate or its extent of protonation, although they do suggest that an acid–base equilibrium is important over the range of [H$^+$] examined.

Interpretation and Discussion

Mechanism.—These data suggest the presence of a dinuclear reaction intermediate involved in a rapid acid–base reaction, with equilibrium quotient *Q*, which we can formulate as

$$VO(OH)_nCr^{4-n} = VO(OH)_{n+1}Cr^{3-n} + H^+ \qquad (3)$$

Since the concentration of this substance is quite small under all conditions studied here, it has not been possible to learn the net charge on either form of the intermediate. There is proposed here a mechanism involving decomposition of the intermediate along two parallel competing paths different by one proton.

$$VO(OH)_{n-1}Cr^{3-n} \xrightarrow{k_0} \text{products} \qquad (4)$$

$$VO(OH)_nCr^{4-n} \text{ (and/or } VO(OH)_{n-1}Cr^{3-n} + H^+) \xrightarrow{k_1} \text{products} \qquad (5)$$

This mechanism leads to the equation

$$-d \ln [\text{int.}]/dt = (k_0Q + k_1[H^+])/(Q + [H^+]) \qquad (6)$$

consistent with the empirical relation, eq. 2.

Spectrum and Acid Dissociation of the Intermediate.—Since the concentration of the intermediate is low and unknown, its absorption spectrum cannot be calculated on an absolute scale. It is possible, however, to obtain relative absorbancy indices, with these calculations dependent on the fraction of reaction proceeding through the intermediate. The assumption made here is that the intermediate carries a negligible portion of the reaction. On this basis $\Delta A/b[Cr^{2+}]_0$ is

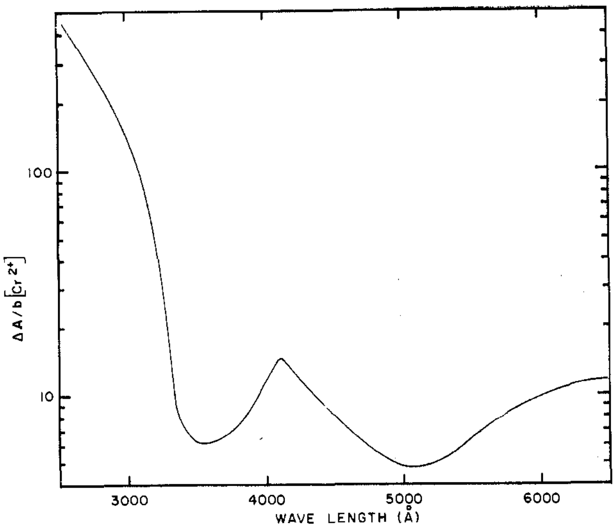

Figure 2.—Illustrating the variation of $A_0/[Cr^{2+}]b$ with wave length. This figure represents the spectrum of the intermediate, with the ordinate directly proportional to its molar absorbancy index.

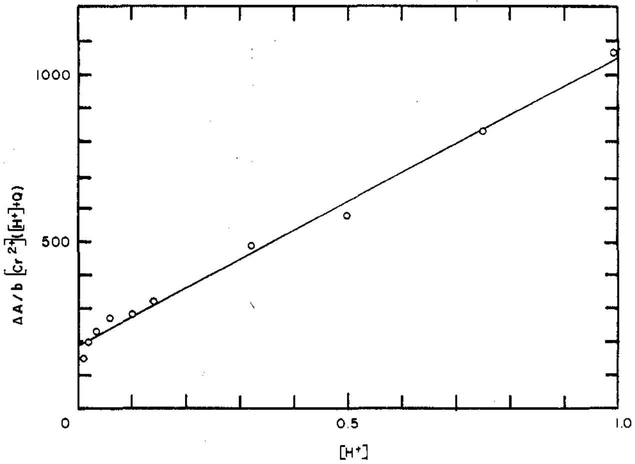

Figure 3.—Illustrating acid ionization of the intermediate. Values of the ordinate were calculated from the data in Table V at 2600 Å. using $Q = 0.74$ M.

TABLE V

ACID DEPENDENCE OF THE ABSORPTION SPECTRUM OF THE INTERMEDIATE

Conditions: 15.0°, Ionic strength 1.00 M ($LiClO_4$), $b = 5.00$ cm.

$[H^+]$, M	$\Delta A/b[Cr^{2+}]$, M^{-1} cm.$^{-1}$ [a] at 3000Å.	at 2600Å.
0.010	172	200
0.020	...	265
0.030	...	302
0.060	...	340
0.100	152	337
0.139	141	364
0.200	145	...
0.320	150	462
0.500	138	465
0.750	138	522
0.990	139	618

[a] The estimated uncertainty in this quantity is *ca.* 8%.

directly proportional to the absorbancy indices of the intermediate. This absorbance difference was obtained by linear extrapolation of the first-order rate data to the time of mixing. Table II presents a typical series of experiments in which reactant concentrations were varied at a particular $[H^+]$ and temperature. Much of the scatter in these data is caused by the necessity of extrapolating the kinetic data to the time of mixing. The constancy of the quantity $\Delta A/b[Cr^{2+}]_0$ eliminates the possibility that the enhanced absorbance is due to a complex formed between the cations and in equilibrium with them. It further eliminates the situation observed for the similar ion VOV^{4+},[7] in which a steady-state concentration of the dinuclear intermediate is maintained by balancing its rates of formation and decomposition. In each of these instances, the absorbance enhancement would be proportional to the product of the V(IV) and Cr(II) concentrations.

Experiments such as these performed at varying wave lengths generate a spectrum of the intermediate. The results of a number of such experiments at 0.200 F $HClO_4$ and 15.0° are shown in Figure 2 in which $\Delta A/b[Cr^{2+}]_0$ is plotted as a function of wave length.

An acid ionization equilibrium was invoked in fitting the hydrogen ion dependence of the decomposition rate; the variation of extent of protonation of the intermediate with changing $[H^+]$ and temperature will lead to corresponding spectral changes. These effects are most evident at wave lengths in the ultraviolet region below 3000 Å. Table V summarizes a number of experiments at 2600 and 3000 Å., in which the values of $\Delta A/b[Cr^{2+}]_0$ were obtained at varying $[H^+]$. In the range of $[H^+]$ covered by these experiments, 0.01–0.99 M, the predominant form of the intermediate changes, since Q at 15.0° is 0.74 M. These data are themselves not sufficient to allow computation of an independent value of Q, but they can be used to check the consistency of these equilibrium measurements with the kinetically derived value. This situation requires that

$$(\Delta A/b[Cr^{2+}])([H^+] + Q) = \alpha[H^+] + \beta Q$$

in which α and β are constants related to the absorbancy indices of the two species and to the fraction of reaction occurring through the intermediate. Figure 3 shows a plot of the left-hand side of this equation *vs.* $[H^+]$ with the value of $Q = 0.74$ M. Although the precision of the data is not sufficiently high to allow any definitive conclusion, the value $Q = 0.74$ M at 15.0° derived from kinetic measurements appears not inconsistent with the observed spectral changes.[14]

Related Reactions.—The mechanisms of formation and decomposition of the intermediate $VO(OH)_nCr^{4-n}$ resemble those found in several related systems, including the dimers Cr(III), V(III), and Fe(III). Table VI summarizes the results of such studies. These reactions between aquo ions constitute the principle examples of cases in which dinuclear intermediates have been demonstrated in 1-equiv. oxidation–

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(14) The large acid ionization quotient for the dimeric ion is not without precedent. The corresponding Q for $Cr(OH)Cr^{5+}$ is 0.024 at 25.0° (ref. 5c).

TABLE VI

COMPARISON OF DECOMPOSITION RATES OF DINUCLEAR METAL ION COMPLEXES

Mode of formation	Dinuclear ion	Specific decompn. rate (25.0°), sec.$^{-1}$	Ref.	log *k* for form. of SCN^- complex[a]
$Cr(IV) + Cr(II)$ and $Cr(III) + OH^-$	$CrOHCr^{5+}$[b]	1.5×10^{-6}[c]	5	Cr(III), −5.7
$Np(VI) + Cr(III)$ and $Np(V) + Cr(II)$	NpO_2Cr^{4+}	2.3×10^{-6}	*e*	Cr(III),[d] −5.7
$V(IV) + V(II)$ and $V(III) + OH^-$	VOV^{4+}	$0.03 + 1.54[H^+]$	7	V(III), +1.8
$V(IV) + Cr(II)$	$VO(OH)_nCr^{4-n}$	$0.018 + 0.645[H^+]$	This work	V(III), +1.8
$Fe(IV) + Fe(II)$ and $Fe(III) + OH^-$	$FeOFe^{4+}$	$0.35 + 3.5[H^+]$	9	Fe(III), +2.1

[a] These entries represent rates of the second-order reaction of M^{3+} and SCN^-; they are values of log *k* (M^{-1} sec.$^{-1}$). Values from ref. 15. [b] The ion $CrOHCr^{5+}$ is not the species formed directly in either reaction, but it is the immediate precursor of Cr^{3+} (ref. 5). [c] In 2.1 *F* $HClO_4$. [d] Cr(III) is more labile than Np(VI) as judged by the rates of H_2O exchange [Cr(III), J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954); **79**, 3343 (1957); Np(VI), S. W. Rabideau and B. J. Masters, *J. Phys. Chem.*, **67**, 2655 (1963)]. [e] J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

reduction reactions of aquo ions. These systems appear unique not so much for the reason that dinuclear intermediates exist, but rather that the intermediates in these cases have lifetimes sufficiently long (except $FeOFe^{4+}$) to be detected by conventional techniques.

To a first approximation the rates of dimer decomposition correlate with the substitution lability of the more labile metal ion component. Table VI compares the rates of decomposition of the intermediates with lability, where the rate[15] of entry of SCN^- in the first coordination sphere of the more labile metal ion component is taken as a measure of the relative substitution lability of the hydrated metal ions.

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(15) M. Eigen and R. G. Wilkins in preprints of "Mechanisms of Inorganic Reactions," a symposium sponsored by the American Chemical Society, Lawrence, Kans., June 1964, p. 75.

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Phenylphosphonitriles. II. Friedel–Crafts Reactions of 2,4,6-Trichloro-2,4,6-triphenyltriphosphonitrile with Benzene

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Reaction of *trans*-2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile with benzene in the presence of $AlCl_3$ can be adjusted to give good yields of 2,4-dichloro-2,4,6,6-tetraphenyltriphosphonitrile or 2-chloro-2,4,4,6,6-pentaphenyltriphosphonitrile. Both *cis* and *trans* isomers can exist for the dichloro compound. These have been isolated and structural assignments have been made. No phenylation of the trichloro compound occurred when $FeCl_3$ or $SnCl_4$ was substituted for $AlCl_3$. Both the *cis* and *trans* isomers of 2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile can be readily isomerized to mixtures of the two by refluxing with $FeCl_3$ in benzene or with $AlCl_3$ in CS_2. Mixtures of all reported phenylphosphonitriles can be analyzed readily by proton n.m.r. spectroscopy applied to their dimethylamido derivatives.

Introduction

Reaction of phosphonitrilic chloride trimer with benzene in the presence of anhydrous $AlCl_3$ was first carried out by Bode and Bach.[1] They obtained good yields of 2,2-diphenyl-4,4,6,6-tetrachlorotriphosphonitrile, but were unable to substitute the phosphonitrilic ring further. More recently, Shaw and Wells[2] found that under the same experimental conditions as employed by Bode and Bach but with longer reflux

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(1) H. Bode and H. Bach, *Ber.*, **75B**, 215 (1942).

(2) (a) R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960); (b) K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).