$$\ln (1 - F) = \ln Q_2 - (q - p)t \qquad (13)$$

Hence

$$k_{app} = -(q - p)/(A + B + C) \qquad (14)$$

In eq. 14 $(q - p)$ is a function of Fe(II) concentration. The theoretical variation of k_{app} with [Fe(II)] at two F^- concentrations was calculated using the theoretical value of $(q - p)$ (as distinguished from the experimental slope) and the results have been plotted as the solid curves I and II in Fig. 2. It is seen that the experimental variation of k_{app} with Fe(II) concentration is in good agreement with the theoretical curve

derived on the basis of the postulated reactions in eq. 4–8. Thus it can be concluded that FeF^{+2} is formed as an intermediate and that isotope exchange occurs between Fe^{+2} and FeF^{+2} rather than between FeF^+ and Fe^{+3} or between Fe^{+2} and an outer coordination sphere complex of Fe^{+3} and F^-. The results do not allow us to distinguish between the bridge or outer-sphere mechanisms of electron transfer.

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Exchange of Ammonia between Hexaamminechromium(III) Salts and Solvent Ammonia. II[1]

BY HANS H. GLAESER AND JOHN P. HUNT[2]

New rate data are reported for the homogeneous ammonia exchange between $Cr^{III}(NH_3)_6$ and liquid ammonia mainly in a perchlorate medium. It is suggested that species such as $Cr(NH_3)_5(NH_2)(ClO_4)^+$ are responsible for the exchange. Further ion association decreases the exchange rate. An apparent activation energy of *ca.* 33 kcal./mole was found. Light appears to speed up the exchange. Addition of benzene to the ammonia causes a reduction in rate. At $-50°$, six ammonia molecules per chromium atom are "held back."

Introduction

We have extended the research reported previously[3] on the $Cr^{III}(NH_3)_6$ exchange system. The former work dealt mainly with nitrate salts, and here we present new data using perchlorate salts which show significant differences in behavior.

Experimental

The procedures and methods used were those described earlier.[3] Anhydrous $NaClO_4$ was prepared by the method of Willard and Smith.[4] Anhydrous $CrCl_2$ was prepared by the method of Schlesinger and Hammond.[5] Care was taken to maintain anhydrous conditions and the runs were made in the dark except for some experiments designed to test these factors.

Results and Treatment of Data

We have not been able to determine the holdback of NH_3 by the Cr(III) ammine species (using nitrate or perchlorate salts) in liquid ammonia at room temperature, but at $-50°$ $Cr(NH_3)_6(NO_3)_3$ is quite soluble and some experiments were performed at this temperature. The procedure was analogous to that used by Hunt and Taube[6] for the $Cr(H_2O)_6^{3+}$ system modified because of the properties of liquid ammonia. Solutions of $Cr(NH_3)_6(NO_3)_3$ in ammonia of normal

isotopic composition (*ca.* 2 *M* in salt) were mixed with liquid ammonia containing *ca.* 1.7 times the normal amount of N^{15}. Solvent was evaporated after 2 and 15 min. intervals, trapped, and converted to N_2 in the usual way. The fractionation on evaporation is small (*ca.* 0.1%). The number of ammonia molecules held back was found to be 6 ± 0.2 per Cr. Since outer-sphere ammonia thus shows no measurable holdback at $-50°$, it seems likely that the holdback is also 6 NH_3/Cr at room temperature. The data below have been treated on this basis. We have confirmed previous observations that packing with glass helices had no effect on the rate. Addition of mercury, which could be a contaminant, also produced no change in exchange rate.

The McKay plots of the exchange data were quite good with the lines passing through the origin. The precision of the data appears to be ±5 to 10%. Values for R (the total exchange rate) were calculated from the relation

$$R = 6[Cr][NH_3]/(6[Cr] + [NH_3]) \times$$
$$(0.693/t_{1/2}) \cong 6 \times 0.693[Cr]/t$$

In the earlier work[3] it was found that the exchange rate was dependent on the concentration of "inert salt" present. This fact raised the question as to how to best control what might be termed "medium effects." The ionic strength is not a useful variable in these experiments because the low dielectric constant of the

(1) Supported by United States Atomic Energy Commisson AT(45-1)-1031.

(2) To whom inquiries may be addressed.

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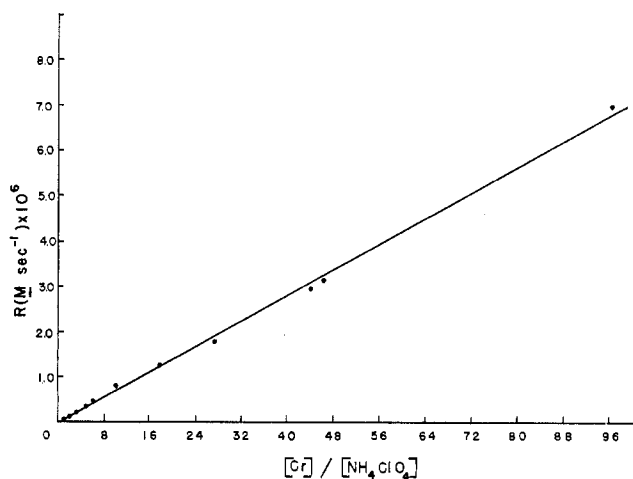(6) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

Fig. 1.—Rate *vs.* chromium and ammonium perchlorate concentrations.

Fig. 2.—Effect of P on exchange rate.

solvent causes extensive ion association, and the necessary equilibrium constants are unknown, making it impossible to calculate ionic strengths. Considering that it is unlikely that ions of other than ± 1 charge are present,[3] we decided to try the expedient of keeping the quantity $[ClO_4^-]_{total} - 2[Cr]$ (designated as P in further discussion) constant. Most of the runs were made using the arbitrary, but convenient, value of $0.068\ M$ for P. Anhydrous $NaClO_4$ was added when necessary to maintain the value for P. In using this approach we are effectively considering all the salts to be 1–1 electrolytes and are keeping their total concentration constant. For our experiments one can also write that $P = [Cr] + [NH_4ClO_4] + [NaClO_4]$. We have not tried to justify this approach theoretically, but we find empirically that it permits reasonable correlations of the rate data with chromium and ammonium perchlorate concentrations. The data given in Table I with $P = 0.068$ are reasonably consistent

TABLE I

EXCHANGE DATA AT 20.54°; $P = 0.068\ M^a$

[Cr(III)], M ($\times 10^2$)	[NH$_4$ClO$_4$], M ($\times 10^3$)	$t_{1/2}$, hr.	R, M sec.$^{-1}$ ($\times 10^6$)
0.50	1.00	16.8	0.345
1.00	0.50	9.5	1.22
1.00	1.00	14.2	0.817
1.00	5.00	85	0.137
1.00	10.0	170	0.068
3.00	0.00	5.0	6.96
3.00	0.50	11.1	3.13
3.00	1.00	19.6	1.78
3.00	5.00	76	0.458
3.00	10.00	140	0.242
5.00	1.00	20.0	2.89

^{a} NaClO$_4$ added when necessary to give listed value of P.

with $R \propto [Cr]/[NH_4ClO_4]$. If P varies appreciably as $[Cr]$ and $[NH_4ClO_4]$ vary, the apparent rate law seems less reasonable. For example, comparison of the fifth and tenth items in Table I shows the rate to be directly proportional to $[Cr]$. Comparison of the third item in Table I with the ninth item (P varies from 0.068 to 2.00) gives an apparent inverse dependence of the rate on $[Cr]$, which seems unlikely. Similarly, com-
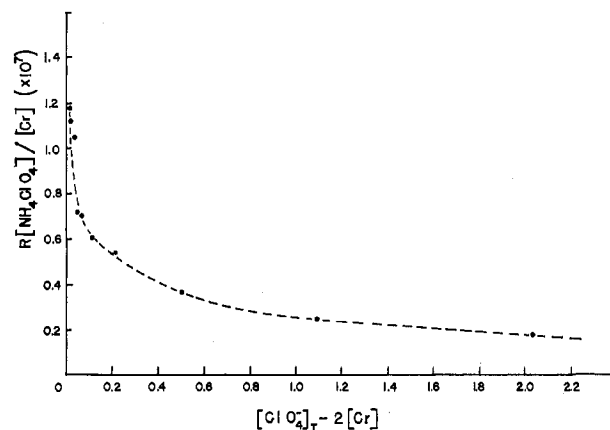
parisons of the effects of changing $[NH_4ClO_4]$ with P constant give essentially the inverse $[NH_4ClO_4]$ effect whereas this is not so if P is not constant. Compare, for example, the seventh and eighth items in Table I with the seventh item in Table II. As can be seen from Table II, these comparisons will vary as P varies.

TABLE II

EFFECTS OF CHANGING PERCHLORATE CONCENTRATION AT 20.54°

[Cr(III)], M ($\times 10^2$)	[NH$_4$ClO$_4$]$_{cor}$, M ($\times 10^3$)	P, M^a	R, M sec.$^{-1}$ ($\times 10^6$)
1.00	1.93	0.012	0.61
1.00	3.86	0.014	0.29
3.00	1.09	0.035	2.90
3.00	1.09	0.045	1.98
3.00	1.09	0.111	1.68
3.00	1.09	0.213	1.49
3.00	1.09	0.500	1.00
3.00	1.09	1.09	0.67
3.00	1.09	2.00	0.48

^{a} NaClO$_4$ added when necessary to give listed value of P.

The data in Table I were treated as for the nitrate experiments.[3] A plot of R *vs.* $[Cr]/[NH_4ClO_4]_{added}$ is linear at high $[NH_4ClO_4]$ and extrapolates through the origin. As before,[3] we assume that the rate behavior (at constant P) is described by the extrapolated line, and we estimate the $[NH_4ClO_4]$ that would have to be present (due to ammonolysis presumably) in the experiment with no added NH_4ClO_4 to give the observed rate. From this estimated concentration we calculate a formal pK for the reaction

$$Cr(NH_3)_6(ClO_4)_n^{3-n} + NH_3 \rightleftharpoons$$
$$Cr(NH_3)_5NH_2(ClO_4)_m^{2-m} + NH_4ClO_4 +$$
$$(n - m - 1)ClO_4^-$$
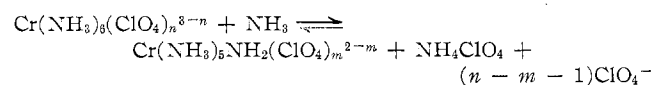
of 5.48 (this can be compared with the value of *ca.* 6 obtained before[3] in the same manner but with $P = 0.01$). Using the value 5.48 we proceed to correct the $[NH_4ClO_4]_{added}$ to give "true" or $[NH_4ClO_4]_{cor}$ values. In Fig. 1 is given a plot of R *vs.* $[Cr]/[NH_4ClO_4]_{cor}$ for $P = 0.068$. The correlation is very good considering the precision of the data and the quite large range of the variables.

As mentioned above, the effects of changing P were investigated and the data are given in Table II. The

TABLE III

MISCELLANEOUS EXPERIMENTS AT 20.54°

[Cr(III)], M ($\times 10^2$)	[NH₄ClO₄], M ($\times 10^3$) (added)	P, M^a	$t_{1/2}$, hr.	R, M sec.$^{-1}$ ($\times 10^6$)	Remarks
3.0	...	0.03	2.45	14.2	...
3.0	...	0.03	0.20	170	$4.1 \times 10^{-3} M$ NaNH₂ added
3.0	...	0.03	0.071	480	$1.0 \times 10^{-2} M$ NaNH₂ added
3.0	1.0	0.068	3.28	10.6	30.01°; E_a = 33 kcal./mole^{-1}
3.0	...	0.03	0.88	39	$4.1 \times 10^{-3} M$ Na added; ppt. formed
3.0	10	0.068	~50	~0.6	Samples exposed to 200-watt light bulb
3.0	0.5	0.068	21	1.7	0.25 M in H₂O
3.0	0.5	0.068	35	1.0	1 M in H₂O
1.0^b	...	...	54	21	0.2 M in H₂O
3.0	0.5	0.068	45	0.76	0.10 M NaNO₃ added
3.0	0.5	0.068	32	1.12	0.10 M NaI added
3.0	...	0.068	5.6	6.2	$7.6 \times 10^{-4} M$ CrCl₂ added
1.0	1.0	0.068	76	0.15	25% benzene–75% NH₃ by vol.
1.0	1.0	0.068	200	0.055	50% benzene–50% NH₃ by vol.

^{a} NaClO₄ added when necessary to give listed value of P. ^{b} NO₃⁻ salt used.

corrected [NH₄ClO₄] values were obtained assuming that the correction would not vary significantly with P. Since the maximum correction is *ca.* 9%, this is a reasonable assumption. In Fig. 2 is shown a plot of $R[NH_4ClO_4]_{cor}/[Cr]$ *vs.* P. An average value (11 runs) of 0.71 is used for the $P = 0.068$ point. The curve is smooth and appears to level off at high P values. A plot of the same function *vs.* $[ClO_4^-]_{total}$ (or $1/[ClO_4^-]_{total}$) does not give a similarly smooth correlation. Such a distinction could not be made for the limited nitrate data.[3]

The results of some miscellaneous experiments are given in Table III. Addition of NaNH₂ (prepared from Na and NH₃) causes a large increase in rate. The values found support the idea, suggested by the inverse NH₄ClO₄ effect, that a $Cr^{III}(NH_3)_5NH_2$ species is responsible for the observed exchange. Using the first entry in Table III we estimate that the concentration of $Cr^{III}(NH_3)_5NH_2$ in this run is $3 \times 10^{-4} M$ assuming the pK for solvolysis is still *ca.* 5.48 when $P = 0.03$ (this may give too large a concentration). If we further assume that the main effect of added NaNH₂ is to remove one proton from $Cr^{III}(NH_3)_6$ for each NH₂⁻ added, the concentrations of $Cr^{III}(NH_3)_5NH_2$ in the second and third runs listed are 4.1×10^{-3} and $1.0 \times 10^{-2} M$, respectively. If R is $\propto Cr^{III}(NH_3)_5NH_2$, we calculate values for R, based on the first entry, of 198×10^{-6} and 470×10^{-6} compared to 170×10^{-6} and 480×10^{-6} observed for the second and third entries.

The single E_a value is the same as found in the nitrate system where only the chromium salt was present.

Addition of a blue, sodium solution gave a brown-black precipitate which appears to be a Cr(II) compound. The apparent increase in rate may be due to some NaNH₂ in the solution.

The rate acceleration by a factor of 2–3 due to light from a 200-watt bulb appears to be real. A control was run to be certain that a rise in temperature was not responsible. This acceleration may be worth further investigation.

Addition of H₂O to either the NO₃⁻ or ClO₄⁻ systems appears to decrease the rate. Some intensifying of color was noted when the water was added. Possibly "NH₄⁺" forms and reduces the rate.

The runs with added sodium nitrate and sodium iodide show again that the exchange rate depends on the nature of the anion present.

CrCl₂ cannot be added in large amounts to the Cr(NH₃)₆(ClO₄)₃ solutions because the Cr(III) salt precipitates as the chloride. Addition of $7.6 \times 10^{-4} M$ CrCl₂ appears to have no significant effect on the exchange rate.

In searching for possible "inert" solvents to mix with ammonia in order to vary the ammonia concentration, it was found that benzene could be used. The addition of benzene clearly reduces the exchange rate. The dielectric constant of benzene is only *ca.* 3, so a simple interpretation is difficult.

Discussion

The data so far obtained on the Cr(III)–NH₃ exchange systems point to a $Cr^{III}(NH_3)_5NH_2$ species as providing the major path for ammonia exchange over a large range of acidity. The anion effects and low dielectric constant of ammonia suggest the importance of an equilibrium of the form $Cr(NH_3)_5(NH_2)(ClO_4)^+ + ClO_4^- \rightleftharpoons Cr(NH_3)_5(NH_2)(ClO_4)_2$ where the "neutral" species is less reactive than the charged one. The lower rates in the nitrate system[3] as compared to the perchlorate system can be rationalized as being due to a greater amount of ion association in the presence of nitrate ion than with perchlorate ion and perhaps also to an inherently lower rate for $Cr(NH_3)_5(NH_2)(NO_3)^+$ than for $Cr(NH_3)_5(NH_2)(ClO_4)^+$. One might expect the planar nitrate ion to interact in a different way than the tetrahedral perchlorate ion with the nearly octahedral chromium complex.

The reduction in rate observed when a mixture of benzene and ammonia is used as solvent is quite likely

due to greater ion association in the medium with lowered dielectric constant. We plan to try other mixed solvents.

The apparent similarity in activation energies for the nitrate and perchlorate systems may be only fortuitous. Eventually more extensive temperature coefficients should be obtained along with much more information concerning the equilibria and their temperature coefficients in these solutions.

The apparent photochemistry would be interesting to investigate further although it would be difficult to obtain quantitative data.

The absence of an effect due to low concentration of Cr(II) suggests that electron transfer may not be appreciably faster in liquid ammonia than in water. We hope to find a more useful salt than $CrCl_2$. Possibly CrI_2 could be used.

We plan to try to extend our studies to other metal ion–ammonia complexes. A wide range of rates has now been discovered (the $Ni^{II}(NH_3)_6$ exchange[7] is very rapid) and some interesting comparisons can be expected.

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The Kinetics of the Chromium(VI)–Arsenic(III) Reaction in Acetic Acid–Acetate Buffer Solutions[1]

By JOHN G. MASON and ALBERT D. KOWALAK[2]

The kinetics of the oxidation of As(III) by Cr(VI) have been investigated over a wide range of As(III) and Cr(VI) concentrations in 0.2 M acetic acid–0.2 M potassium acetate buffers and a constant ionic medium of 1.5 M adjusted with potassium nitrate. In regions where the As(III) greatly exceeds the Cr(VI) the rate law is $-d[Cr(VI)]/dt = kK[As(III)][Cr(VI)]/(1 + K[As(III)])$ where K can be identified as the equilibrium constant for the reaction As(III) $+ HCrO_4^- \rightleftharpoons$ As(III)·$HCrO_4^-$ and k is the specific rate constant for the decomposition of the complex. At high concentrations of Cr(VI), a second path involving $Cr_2O_7^{2-}$ appears.

Introduction

The paths by which As(III) is oxidized by one- and two-equivalent reagents have been the subject of much discussion,[3] most of which is concerned with the possibility of As(IV) as an intermediate. Recently, Woods, *et al.*,[4] have studied the induced oxidation of As(III) by the Fe(II)–persulfate system in the absence and presence of oxygen. They conclude that As(IV) is produced as an intermediate in these reactions. Csanyi postulated As(IV) as an intermediate in the titration of a mixture of persulfate and hydrogen peroxide with one-equivalent oxidants[5] and in the induced reduction of chlorate by arsenite.[6] Mechanisms involving As(IV) as an intermediate have been postulated for the oxidation of As(III) initiated by X-rays[7] and in the photosensitized reaction between arsenite and hydrogen peroxide.[8]

The oxidation of As(III) by Cr(VI) in acid solution was studied many years ago by DeLury,[9] whose data

have been discussed and interpreted by Westheimer[10] and Edwards.[11] The evaluation of Edwards leads to the rate law

$$R = k_a[HCrO_4^-][H_3AsO_3][H^+] + k_b[HCrO_4^-][H_3AsO_3][H^+]^2$$

which is analogous to the rate law for the oxidation of isopropyl alcohol by chromic acid.[12] Westheimer,[10] from a detailed analysis of the induced oxidation of Mn(II), concludes that Cr(IV) is the unstable oxidation state of chromium produced in this reaction and that the formation of As(IV) is improbable.

Kolthoff and Fineman[13] studied the reaction in alkaline buffers and reported the rate law $R = k[As(III)][Cr(VI)]$ with no dependence upon $[H^+]$ indicated above a pH of 9. They speculate that there should then be a series of terms varying with $[H^+]$ to describe the whole region from acid to alkaline solution.

This work was initiated to investigate the possibility of As(IV) as an intermediate in this reaction, determine the role of hydrogen ion more specifically, and test for general acid catalysis. Preliminary work indicated that the reaction appeared to be independent of hydrogen ion over the pH region 4.3 to 5.5 but dependent upon the concentration of acetic acid. Because of

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant AF-AFOSR-210-63.
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