

seems unlikely that P would differ from unity by more than 0.02, and the shift in $(N/X_{N'})$ ascribable to such a P is only ± 0.0002 . P may not be unity, but its deviation from unity is not the source of the discrepancy under discussion.

It seems much more likely that the results of experiments with a high ratio of reagent concentrations are in error, the most likely source of error being the occurrence of side reactions which are irreproducible in effect under the conditions employed. We have examined a number of possibilities (hydrolyses and solvation equilibria of reagents and products, etc.), and none seem to account for both the direction and magnitude of the discrepancy between the equal and unequal concentrations experiments or are ruled out on the basis of relative rate^{4,5,23} or would produce products easily detectable and identifiable on the analytical chromatogram of the reacted samples.

(23) E. A. Moelwyn-Hughes, *Proc. Roy. Soc. (London)*, **164A**, 295 (1938); **196A**, 540 (1949); **220A**, 386 (1953).

Actually, the least-squares *calculated* values of $(N/X_{N'})$ average only 0.0047 ± 0.0047 higher than the least-squares *experimental* values; though this is a difference in isotope effect of $14 \pm 14\%$, on the average, it is not very large. It is not possible, on the evidence available, to ascribe to either (k_1/k_2) or (k_1/k_3) the major part of the discrepancy. It is not to be expected that this state of affairs would be general to the application of the high concentration-ratio technique. Some insight into the experimental limitations operating in the cyanization of methyl iodide may be obtainable from studies on the cyanizations of methyl bromide and methyl chloride, and we have projected such investigations. Additionally, these would furnish further information as to "leaving group" effects, including the effect of "particle" mass.

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Kinetics of Some Electron Transfer Reactions of Cobalt(III)

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The rates of reaction of V_{aq}^{++} with complexes RL ($R = Co^{III}(NH_3)_6$; $L = OH_2, NH_3, Cl^-$) have been studied in H_2O and in D_2O . The rate of reaction of Cr_{aq}^{++} with RNH_3^{+++} has been studied in the two media. Rates, ligand and isotope effects are compared with those found in reactions, the nature of whose activated complexes are more definitely understood.

Cr(II), both as an aquo ion and as the tris- α, α' -bipyridine complex, has received much attention as a reductant for Co(III) complexes of the type RL . These reactants have been shown to exemplify two kinds of activated complexes. $Cr(bip)_2^{++}$ ($bip = \alpha, \alpha'$ -bipyridine) has been found to react by an outer sphere activated complex, the coordination spheres of both oxidant and reductant apparently remaining intact in the activated complex,¹ while Cr_{aq}^{++} has been shown to exploit the bridged activated complex² (for $L = OH^-, OH_2, SCN^-, NO_3^-, PO_4^{=}, acetate, oxalate, etc.$), wherein the one ligand on the oxidant which is not NH_3 occupies a coordination position of each metal center in the activated complex.

The demonstration of the operation of the bridged activated complex depends upon the slowness with which Cr(III) complexes reach substitution equilibrium. V(III) rapidly equilibrates with solution, and thus the mechanism of reaction of V_{aq}^{++} cannot be determined by the methods which availed for Cr_{aq}^{++} . An attempt is here made to elucidate the mechanism of reaction of V_{aq}^{++} with complexes of Co(III) by arguments based upon the chemical and isotopic effects characteristic of the two activated complexes as calibrated by Cr(II). The reaction of Cr_{aq}^{++} with RNH_3^{+++} has been studied for inclusion in the comparisons.

(1) A. Zwickel and H. Taube, *Discussions Faraday Soc.*, in press (1960).

(2) H. Taube, "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1959, Chapter 1.

Experimental

The reductants are air-sensitive and all work was done in an atmosphere of nitrogen scrubbed by Cr_{aq}^{++} to remove any traces of oxygen. Cr_{aq}^{++} was generated both electrolytically and by reduction with amalgamated zinc. The solutions of Cr(III) were prepared by reducing a solution of recrystallized potassium dichromate with hydrogen peroxide. V_{aq}^{++} was generated by reduction with amalgamated zinc of solutions of V(IV) which were obtained by reaction of vanadium pentoxide with hydrochloric acid. The vanadium pentoxide was prepared by roasting recrystallized ammonium metavanadate. Crystalline vanadyl perchlorate, prepared by W. J. Pendergast, was also used as source of V(IV). The Co(III) compounds were prepared by standard methods.

The reductant was added to deoxygenated solutions containing oxidant, neutral salt to maintain the ionic strength and other reactants (*e.g.* acid). The mixture was stirred by bubbling with nitrogen and pumped into a deoxygenated spectrophotometer cell, the cell and the mixing vessel being thermostatted by immersion in a water-bath. After filling, the cell was isolated, dried and transferred to the thermostatted cell compartment of a Cary Model 14 spectrophotometer, where the optical density of the solution was recorded as a function of time at a chosen wave length. One of the maxima in the visible region of the Co(III) complex was used in all cases. After appropriate correction for absorption by species other than Co(III), the second order rate law (first order in oxidant and in reductant) was used in the form

$$\frac{d}{dt} \ln \frac{(V^{++})}{(Co^{III})} = -k(Co_0^{III} - V_0^{II})$$

the differentiation being performed graphically. Linearity of plots of the logarithmic ratio *vs.* time was taken as evidence of the validity of the treatment of data and specifically of the second order rate law. The wave lengths chosen and extinction coefficients used are shown in Table I.

TABLE I

Oxidant	WAVE LENGTHS AND EXTINCTION COEFFICIENTS USED IN DATA ANALYSIS							
	Wave length, μ	ϵ_{CoIII}	ϵ_{CoII}	ϵ_{VIII}	ϵ_{VII}	$\epsilon_{\text{O}_2\text{Cl}^{++}}$	$\epsilon_{\text{Cr}^{+++}}$	$\epsilon_{\text{Cr}^{++}}$
RNH_3^{+++}	475	55.0	3.0	1.1	1.3	8.1	3.1	0.4
RCl^{++}	530	48.0	3.7	3.2	3.6
ROH_2^{+++}	345	44.1	0.1	2.1	2.8
ROH_2^{+++}	490	47.0	3.9	1.7	2.0

When, as was frequently the case, the specific rate k was found to depend on chloride concentration, the dependence was determined by the method of least squares.

Results

The specific rates of reactions of RNH_3^{+++} with $\text{V}_{\text{aq}}^{++}$ and with $\text{Cr}_{\text{aq}}^{++}$ obey the law

$$k = [k_1 + k_2(\text{Cl}^-)]$$

The kinetic data obtained at ionic strength 0.40 are plotted in Figs. 1 and 2; the constants abstracted from the plots are given in Table II.

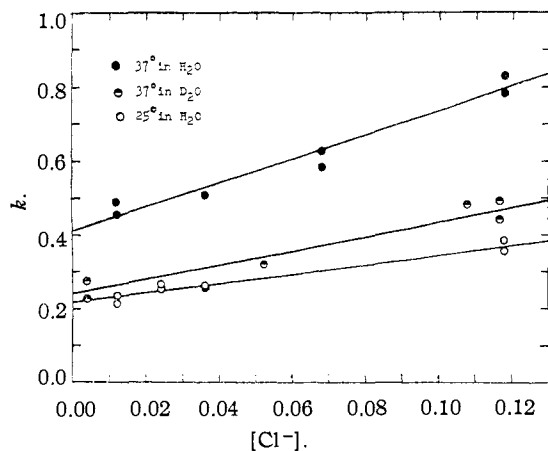


Fig. 1.—Specific rates for $\text{RNH}_3^{+++} + \text{V}_{\text{aq}}^{++}$.

The activation parameters calculated from the Eyring equation are given in Table III.

TABLE II

Reductant	RNH_3^{+++} AS OXIDANT		
	Temp., °C.	$k_1, M^{-1} \text{min.}^{-1}$	$k_2, M^{-1} \text{min.}^{-1}$
$\text{Cr}_{\text{aq}}^{++}$	25.0	0.0053	0.74
	37.0	.014	1.70
	37.0	.011 ^a	1.35 ^a
$\text{V}_{\text{aq}}^{++}$	25.0	.22	1.27
	37.0	.41	3.27
	37.0	.24 ^a	1.95 ^a

In 98% D_2O ; the values of k recorded have been corrected to 100% D_2O using a linear extrapolation.

TABLE III

ACTIVATION PARAMETERS FOR RNH_3^{+++} REACTIONS			
Reductant	Path	ΔH^\ddagger (kcal.)	ΔS^\ddagger (e.u.)
$\text{Cr}_{\text{aq}}^{++}$	k_1	14.7	-30
$\text{Cr}_{\text{aq}}^{++}$	k_2	12.4	-25
$\text{V}_{\text{aq}}^{++}$	k_1	9.1	-40
$\text{V}_{\text{aq}}^{++}$	k_2	14.1	-20

The product of reaction of $\text{Cr}_{\text{aq}}^{++}$ by the chloride-dependent path shown to be $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{++}$, both spectrophotometrically and by determining the free chloride by precipitating it as AgCl .

The reaction of $\text{V}_{\text{aq}}^{++}$ with RCl^{++} was studied at ionic strength 1.00 at 25°. The chloride-de-

pendence of the rate of this reaction was not studied, but the lack of curvature in the rate plots indicates that the low levels of chloride generated as reaction proceeded (*ca.* 0.001 M) did not sensibly affect the rate. In H_2O , the specific rate under the above conditions was found to be 342 $M^{-1} \text{min.}^{-1}$. In 74% D_2O , with $(\text{NH}_3)_5\text{CoCl}^{++}$ as reactant, a specific rate of 202 was found; in 85% D_2O , the specific rate using $\text{Co}(\text{ND}_3)_5\text{Cl}^{++}$ as oxidant was measured as 156. The variation in deuterium concentration is too great to permit detailed inferences to be drawn from these latter numbers, but it may be stated that the protonated and deuterated species react at approximately the same rate and that this rate is, in 100% D_2O , a factor of about 2.6 lower than the rate in H_2O .

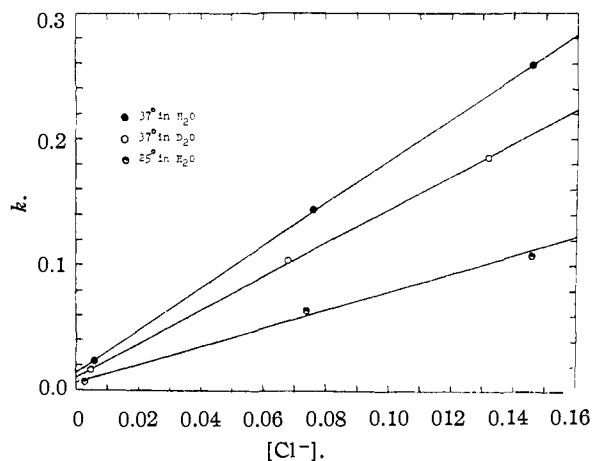


Fig. 2.—Specific rates for $\text{RNH}_3^{+++} + \text{Cr}_{\text{aq}}^{++}$.

The reaction of $\text{V}_{\text{aq}}^{++}$ with ROH_2^{+++} was exhaustively studied at 25° at ionic strengths of 1.00 and 1.20. At ionic strength 1.00 in perchlorate medium, at acidities ranging from 0.06 to 0.90 M , the results of 16 runs scatter randomly between the limits $k = 26 M^{-1} \text{min.}^{-1}$ and $k = 52 M^{-1} \text{min.}^{-1}$, there being no discernible trend with acidity. At ionic strength 1.20 (by perchlorate-chloride), there is again no trend with acidity, but the data, plotted in Fig. 3, do indicate that the rate expression is

$$\text{rate} = [k_1 + k_2(\text{Cl}^-)] (\text{V}_{\text{aq}}^{++})(\text{ROH}_2^{+++})$$

with $35 < k_1 < 65$ and $115 < k_2 < 170$. Only the limiting values of k obtained from 16 runs at zero chloride are plotted. A single run in 94% D_2O at ionic strength 1.00 at 25° in perchlorate medium gave a constant of 10.3.

The cause of the scatter in the results is unknown. Several separate and distinct preparations of all reagents were used. Traces of fluoride, sulfate and chromous ions (*ca.* $10^{-4} M$) were added without altering the usual random behavior. Similar difficulties indicating catalysis by trace impurities had

previously been encountered in the study of this oxidant with $\text{Cr}_{\text{aq}}^{++}$.³ There, the difficulty was traced to a stirring bar which had a leaky jacket.

Discussion

The lack of acid dependence of the rate of reaction of $\text{Cr}_{\text{aq}}^{++}$ with RNH_3^{+++} indicates that no protons are dissociated from the coordinated ammonia molecules prior to forming the activated complex; an equilibrium involving dissociation preceding the rate determining step would lead to an inverse dependence of rate on acidity. Thus, it is unlikely that NH_2^- bridges are formed. Since NH_2 has no orbitals sufficiently low-lying for use in bonding to the reductant in the activated complex, a bridged activated complex is *a priori* most unlikely. The catalysis of this reaction by chloride indicates that the mechanism differs from that usually found with this reductant, since none of the many reactions of $\text{Cr}_{\text{aq}}^{++}$ previously studied, all of which proceed through a bridged activated complex, shows evidence of chloride catalysis, at least at 0.1 M concentrations. Thus, it appears that this reaction proceeds through an outer sphere activated complex.

The results obtained for $\text{V}_{\text{aq}}^{++}$ as reducing agent may profitably be examined in their relationship to the results obtained with the two reducing agents having known mechanisms of attack, *i.e.*, $\text{Cr}_{\text{aq}}^{++}$ and $\text{Cr}(\text{bip})_3^{++}$. Rates of reaction for these reductants with several oxidants relative to $\text{Co}(\text{NH}_3)_6^{+++}$ are presented in Table IV.

TABLE IV

Oxidant	RELATIVE RATES		
	$\text{Cr}_{\text{aq}}^{++}$	$\text{V}_{\text{aq}}^{++}$	$\text{Cr}(\text{bip})_3^{++}$
$\text{Co}(\text{NH}_3)_6^{+++}$	1	1	1
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{+++}$	6.0×10^3	135	91
$\text{Co}(\text{NH}_3)_5\text{OH}^{++}$	2×10^{10}	$< 10^7$	50
$\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$	$> 10^6$	1.6×10^3	1.5×10^3

Only an upper limit can be set on the relative rate of reaction of $\text{V}_{\text{aq}}^{++}$ with $\text{Co}(\text{NH}_3)_5\text{OH}^{++}$; no acid dependence was observed over a range of acidity which changes the rate of reaction of $\text{Cr}_{\text{aq}}^{++}$ with $\text{Co}(\text{NH}_3)_5\text{OH}_2^{+++}$ by a factor of 40, from 40 to $1600 \text{ M}^{-1} \text{ min}^{-1}$. This factor was used in setting the limit; the actual specific rate may be far lower. With this understanding, the rate ratios for $\text{V}_{\text{aq}}^{++}$ parallel those for $\text{Cr}(\text{bip})_3^{++}$ remarkably closely. The isotope effects found for the various reactions are tabulated in Table V. The rather large factor found for the reaction of $\text{V}_{\text{aq}}^{++}$ with $\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$ contrasts markedly with that found for the reaction of $\text{Cr}_{\text{aq}}^{++}$ with $\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}$, a reaction known to proceed through a bridged activated complex.⁴

It is interesting to note that all the reactions of $\text{V}_{\text{aq}}^{++}$ studied evidence chloride catalysis, a phenomenon not found at all with $\text{Cr}(\text{bip})_3^{++}$ and found at comparable concentrations for $\text{Cr}_{\text{aq}}^{++}$ only with $\text{Co}(\text{NH}_3)_6^{+++}$, when the outer sphere activated complex is required. It is apparent that chloride, to function as catalyst, must be intimately associated with either oxidant or reductant, and the former possibility is here precluded by the

(3) A. Zwickel and H. Taube, *THIS JOURNAL*, **81**, 1288 (1959).

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

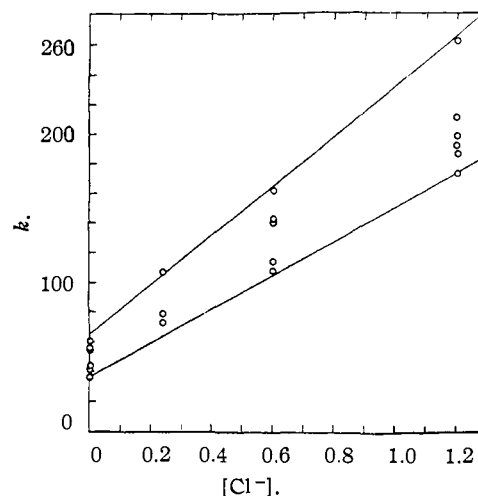


Fig. 3.—Specific rates for $\text{ROH}_2^{+++} + \text{V}_{\text{aq}}^{++}$.

nature of the oxidants. The reactions of $\text{Cr}(\text{bip})_3^{++}$ are not catalyzed by chloride, but here incorporation of chloride into the first coordination sphere of the reductant would entail loss of bipyridine. Presumably, the function of chloride as catalyst is to bring electrons to the surface of the reductant; this bipyridine can do more efficiently than chloride which in turn is more efficient than H_2O .

TABLE V

THE EFFECT OF THE SOLVENT CHANGE $\text{H}_2\text{O}-\text{D}_2\text{O}$ ON RATES

Oxidant	Reduct.	$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}}$
$\text{Co}(\text{NH}_3)_6^{+++}$	$\text{Cr}(\text{bip})_3^{++}$	0.98
$\text{Co}(\text{NH}_3)_6^{+++}$	$\text{Cr}_{\text{aq}}^{++}$	1.3
$\text{Co}(\text{NH}_3)_6^{+++}$	$\text{V}_{\text{aq}}^{++}$	1.7
$\text{Co}(\text{NH}_3)_5\text{OH}_2^{+++}$	$\text{Cr}(\text{bip})_3^{++}$	2.6
	$\text{Cr}_{\text{aq}}^{++}$	3.8 ⁵
	$\text{V}_{\text{aq}}^{++}$	2.6
$\text{Co}(\text{NH}_3)_5\text{Cl}^{++}$	$\text{V}_{\text{aq}}^{++}$	2.2
$\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}$	$\text{Cr}_{\text{aq}}^{++}$	1.3 ⁴

The demonstration that Cl^- is an effective catalyst even when it cannot make a bond to the oxidizing agent is important, if for no other reason than this: that the mere fact of catalysis by Cl^- , etc., cannot be taken as evidence of a bridged activated complex. Thus the arguments² which have been used to infer that the reactions of $\text{Cr}_{\text{aq}}^{++}$ with $\text{Fe}(\text{III})$ and of $\text{Fe}_{\text{aq}}^{++}$ with $\text{Fe}(\text{III})$ proceed by bridged activated complexes are vitiated. The arguments were based on the fact⁵ that Cl^- is not an efficient catalyst for the reaction between $\text{RH}_2\text{O}^{+++}$ and $\text{Cr}_{\text{aq}}^{++}$ but is for that between $\text{Fe}(\text{III})$ and $\text{Cr}_{\text{aq}}^{++}$. The difference in substitution lability of the Fe^{+++} and Co^{+++} centers was invoked to explain the difference in behavior. But the difference between the systems may in fact be this: when $\text{RH}_2\text{O}^{+++}$ and $\text{Cr}_{\text{aq}}^{++}$ react, a bridged activated complex is certainly involved⁶ with H_2O as bridging group so there is no great benefit to placing Cl^- in the coordination sphere of $\text{Cr}_{\text{aq}}^{++}$; when Fe^{+++} and Cr^{++} react, the activated complex may be of the outer sphere type and the process is bene-

(5) R. K. Murmann, H. Taube and F. A. Posey, *ibid.*, **79**, 262 (1957).

(6) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).

fit by Cl^- in the same way as is the reaction between $\text{Co}(\text{NH}_3)_6^{+++}$ and Cr^{++} . A careful quantitative study of the catalysis by anions as a function of temperature may however lead to a means of distinguishing between the two kinds of activated complexes. Newton⁷ has suggested that there may be a systematic difference in the entropies of activation for reactions having the activated complexes $[\text{M}_1\text{X M}_2]_{\text{aq}}^{+p}$ and $[\text{M}_1(\text{H}_2\text{O})_n (\text{H}_2\text{O})_m \text{M}_2\text{X}]^{+p}$ (both referred to reactants in the same state) and the point is well worth a detailed investigation.

The mechanism of reaction of $\text{V}_{\text{aq}}^{++}$, which seems more closely to approximate to the outer sphere than to the bridged activated complex, must in the last analysis be explicable on electronic grounds. "The" electron which is transferred from $\text{V}_{\text{aq}}^{++}$ resides in a t_{2g} orbital; d orbitals of this symmetry type maximize along axes perpendicular to the faces of the coordination octahedron. Thus, sigma overlap of reductant orbitals with the acceptor orbital (presumably the d_z^2 orbital of $\text{Co}(\text{III})$) is facilitated by attack of the ligand of the oxidant most "permeable" to electrons at a face of the coordination octahedron of the reductant. With $\text{Cr}_{\text{aq}}^{++}$ as reductant, the electron which is to transfer resides in an e_g orbital, say d_z^2 , and a bridged

(7) T. W. Newton, private communication.

activated complex is required to provide sigma overlap with the d_z^2 orbital of the oxidant.

It is interesting (and it may be productive) to speculate on the origin of the scatter in the rate measurements for the system $\text{V}_{\text{aq}}^{++} + \text{Co}(\text{NH}_3)_5\text{OH}_2^{+++}$. The factor of 2 in scatter can be explained by the reaction sequence

1. $\text{Co}^{\text{III}}(t_{2g}^6) + \text{V}^{\text{II}}(t_{2g}^3) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{V}^{\text{III}}(t_{2g}^2)$
2. $\text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{Co}^{\text{III}}(t_{2g}^6) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2) + \text{Co}^{\text{III}}(t_{2g}^6e_g)$
3. $\text{Co}^{\text{III}}(t_{2g}^5e_g) + \text{V}^{\text{II}}(t_{2g}^3) \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2) + \text{V}^{\text{III}}(t_{2g}^2)$
4. $\text{Co}^{\text{II}}(t_{2g}^5e_g) + \text{M} \longrightarrow \text{Co}^{\text{II}}(t_{2g}^5e_g^2)$
5. $\text{Co}^{\text{III}}(t_{2g}^5e_g) + \text{M} \longrightarrow \text{Co}^{\text{III}}(t_{2g}^6)$

If reaction 1 is rate-determining in all cases, and either reaction 4 or 5, de-excitation by some adventitious impurity, is much faster than reaction 2 and 3, the observed rate will be the rate of 1. Contrarywise, if reactions 2 and 3 are rapid compared to the de-excitations 4 and 5, the observed rate will be twice that of 1. Scatter is to be understood on the basis of a competition between de-excitation and energy transfer leading to reaction.

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Kinetics of Liquid Phase Hydrogenation. II. Hydrogenation of Aromatic and Aliphatic Nitrocompounds Over A Colloidal Platinum Catalyst

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The rate of hydrogenation of para-substituted nitrobenzene over colloidal platinum obeys the same kinetic equation found applicable to the hydrogenation over colloidal rhodium and palladium catalysts.¹ The hydrogenation of aliphatic nitrocompounds seems to be poisoned by the reaction products. Another difference is that with the addition of acid or base the rate of hydrogenation of aromatic nitrocompounds increases whereas the rate for aliphatic nitrocompounds decreases.

Introduction

In the first part of this kinetic study of liquid phase hydrogenation,¹ the reaction characteristics of the hydrogenation of aromatic nitrocompounds over colloidal rhodium and palladium catalysts have been described. A kinetic equation was derived and found to be in good agreement with all the results found in the reactions studied. The present investigation is designed to extend the same kinetic study to hydrogenation reactions over colloidal platinum. For the reaction substrate, aromatic nitrocompounds and a few aliphatic nitrocompounds were used.

Experimental and Results

Apparatus and Procedures.—The same apparatus and experimental procedures as that described previously¹ were used.

Preparation of the Catalyst.—The solution of platinum chloride containing 0.5 mg. of Pt per ml. of solution was prepared by dissolving either platinum chloride or 10% solution of H_2PtCl_6 in 1% polyvinyl alcohol (PVA) aqueous solution.

(1) Hsien-Cheng Yao and P. H. Emmett, *THIS JOURNAL*, **61**, 4125 (1959).

To 500 ml. of this solution, 3 ml. of 10% NaOH solution was added; the solution was then brought to a boil for a few minutes. After the solution was cooled down to 0° in an ice bath, 0.2–0.3 ml. of hydrazine hydrate was added. The solution was then shaken and gradually warmed to room temperature. The brown solution did not change appearance in the first few minutes; then the color became darker followed by a sudden change to a black color with evolution of gas. It was then boiled for 10 minutes and stored for use.

Determination of Reaction Order with Respect to Aromatic Nitrocompounds.—The rates of hydrogenation of aromatic nitrocompounds were determined under constant pressure of hydrogen. The following factors which were found to affect the order of reaction were studied by varying only one particular factor and maintaining the other conditions constant in each series of experiments.

1. **The Amount of Catalyst.**—In a series of seven experiments only the amount of catalyst used was varied. The amount of Pt in 100 ml. of aqueous solution containing 0.002322 mole of *p*-nitrophenol ranged from 0.5 to 20 mg. The results of a series of experiments in neutral solutions are plotted according to zero order kinetics with respect to the substrate in Fig. 1. Similar results were obtained in a parallel series of experiments under the same conditions but in solutions made acidic by the addition of 1 ml. of 70% HClO_4 . It was found that the reaction order with respect to the nitrocompound changes from first to zero order with increasing amount of catalyst. The amounts of platinum at