tion at the N.A.C.A. Lewis laboratory. One phase of this general program has been concerned with the influence of molecular structure on the burning velocities of hydrocarbon–air mixtures. The present work on the acetylene derivatives should allow further insight into these phenomena.

Burning velocities were measured in an open burner type apparatus[1] at a pressure of 1 atmosphere. Burning velocity of isopropenyl acetylene was measured at an initial mixture temperature of 298°K. The high boiling point of diisopropenyl acetylene required that the burning-velocity determinations be made at elevated initial mixture temperatures. Consequent calculation of temperature dependence of the burning velocity ($u_f \alpha T_i^{1.46}$) permitted extrapolation[1] of the measured quantity to T_i = 298°K. This value is given in parentheses in Table I. Experimental values of maximum burning velocity and the concentrations at which these maxima occur are listed in Table I. The burning velocities of both compounds are consistent with previously discussed[1] structure relationships.

TABLE I

Compound	T_i (°K.)	u_f(max.) (cm./sec.)	% Stoichiometric at maximum
Isopropenyl acetylene	298	62.0	105
Diisopropenyl acetylene	425	88.0	105
Diisopropenyl acetylene	377	74.0	105
Diisopropenyl acetylene	(298)	(52.3)	105

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The Effect of Cyanide on the Rate of the Thallous–Thallic Exchange Reaction[1,2]

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In a number of studies of the kinetics of electron transfer exchange reactions between metal ions in aqueous solution it has been found that the rates are affected significantly by the presence of anions which are capable of forming complexes with one of the reactants. Indeed such an anion effect is so general that it may be considered a characteristic feature of these oxidation–reduction exchange reactions. Thus for example, the rates of the thallous–thallic,[4–6] cerous–ceric,[7,8] ferrous–ferric,[9,10] europous–europic[11] and antimonous–antimonic[12,13] exchanges are altered, in some cases greatly, when the anionic composition of the solution is changed. Corresponding effects are also found frequently in non-equilibrium oxidation–reduction.

In the case of exchange between thallium(I) and thallium(III) in aqueous solution it is known that the rate is affected by nitrate[4] and is very sensitive to chloride.[5,6] The purpose of the present work was to study the effect of cyanide on this reaction in perchlorate–cyanide mixtures.

Experimental

The exchange reaction was followed by means of radioactive thallium, Tl^{204}, obtained from Oak Ridge. The irradiated thallous nitrate was dissolved in distilled water, and thallous perchlorate was precipitated with perchloric acid. The salt was purified by several successive recrystallizations from distilled water. The final product was dissolved in distilled water to give a stock solution of radioactive thallous perchlorate. The specific activity was determined to be 2.3 microcuries per milligram of thallium. A test for nitrate, with brucine, was negative.

A stock solution of inactive thallous perchlorate was prepared in the fashion just described, starting with reagent grade thallous perchlorate.

The thallic perchlorate stock solution was prepared electrolytically[14,15] from a solution of purified thallous perchlorate in perchloric acid. The final acidity was 2.86 *f*. A test for chloride with silver nitrate (0.5 *f* in the mixture) was negative.

The other reagents used were C.P. or reagent grade.

Reaction mixtures were prepared by mixing in a volumetric flask the appropriate amounts of stock solutions containing $TlClO_4$, $Tl(ClO_4)_3$. $HClO_4$, $NaClO_4$ and NaCN. The reaction mixtures were made up to a nominal ionic strength of approximately 0.5. Exact values of the ionic strength cannot be calculated since the equilibrium constants for the formation of the thallium–cyanide complexes are unknown. The values are believed to lie in the range 0.4–0.55 mole/l., except in one case as noted in Table I. Variations in this range are not expected to have an important effect on the rate.

The reaction mixture was maintained at 30.0 ± 0.1° in a water-bath. At intervals aliquots were pipetted from the reaction mixture. Each aliquot was combined with 10 mg. of Tl^+ carrier. and thallous chromate was precipitated as earlier described.[5] The precipitates were mounted in the form of 1 inch diameter discs on filter paper, and were counted on a gas-flow proportional counter.

Results and Discussion

The results were analyzed in terms of the McKay formula[14,15] in the usual way. The expression used was

$$\ln \frac{y - y_\infty}{y_0 - y_\infty} = -\frac{R}{ab}(a + b)t$$

where y is the activity of the initially active form (thallous) at time t, y_0 and y_∞ are the activities of the thallous fractions at times zero and infinity respectively, a and b are the over-all concentrations

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[1] Work supported in part by the U. S. Atomic Energy Commission.

[2] A more detailed account of this investigation will appear in *Eugenharia e Quimica* (Rio de Janeiro).

[3] On leave from the Oswaldo Cruz Institute, Rio de Janeiro, Brazil.

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[15] We are indebted to Dr. R. W. Stoenner for this preparation.

TABLE I

THALLOUS-THALLIC EXCHANGE IN THE PRESENCE OF CYANIDE AT 30° AND IONIC STRENGTH *ca.* 0.5

$(\Sigma CN^-)/(Tl(III))$	Tl(III), $f \times 10^2$	Tl(I), $f \times 10^2$	NaCN, f	$HClO_4$, f	$NaClO_4$, f	$t_{1/2}$, hr.	k, f^{-1} hr.$^{-1}$	$k_{predicted}$ f^{-1} hr.$^{-1}$
0	0.588	0.318	0	0.500	0	104	0.74	
0.1	1.38	.812	0.00138	.460	0	52	.61	0.66
.2	1.47	1.40	.00294	.420	0	40	.60	.60
.3	1.38	0.812	.00413	.460	0	61	.52	.53
.4	1.38	.812	.0055	.460	0	78	.40	.46
.5	0.588	.318	.00294	.500	0	208	.36	.40
.7	1.38	.812	.00964	.460	0	115	.275	.296
1.0	0.588	.318	.00588	.500	0	465	.164	.163
1.2	1.38	1.40	.0615	.440	0	222	.112	.097
1.7	2.41	1.40	.0410	.357	0	1700[a]	.0107	.0111
2.0	2.31	0.170	.0345	.350	0	2900[a]	.0096	
2.5	2.41	1.40	.0603	.330	0	>2300	< .008	
3.0	2.31	0.170	.069	.327	0	7800[a]	.0036	
5.0	2.41	1.40	.120	.290	0	>4000	< .005	
8.0	2.41	1.40	.193	.200	0	>2300[b]	< .008	
17.0	0.588	0.318	.100	0	0.400	368	.207	
25.8	.588	.318	.152	0	.300	105	.73	
34.0	.588	.318	.200	0	.300	45	1.70	
44.0	.588	.318	.257	0	.200	17.3	4.4	
68.0	.588	.318	.400	0	.100	4.12	18.5	
85.0	.588	.318	.500	0	0	1.68	46	

[a] Some decomposition in reaction mixture. [b] Ionic strength about 0.33 mole/l.

of the two exchanging substances, and R is the constant rate at which the exchange occurs under the given conditions. The quantity y_0 was calculated from data on the stock solution: in some cases it was also checked by reducing an aliquot of the reaction mixture with SO_2, precipitating the thallium as thallous chromate, and counting. Results obtained by the two methods agreed. The quantity y_∞ was determined in some cases by allowing the exchange reaction to proceed to equilibrium; in most cases, in which the long half-time made this approach inconvenient, it was calculated from the expression

$$y_\infty = y_0 \frac{b}{a + b}$$

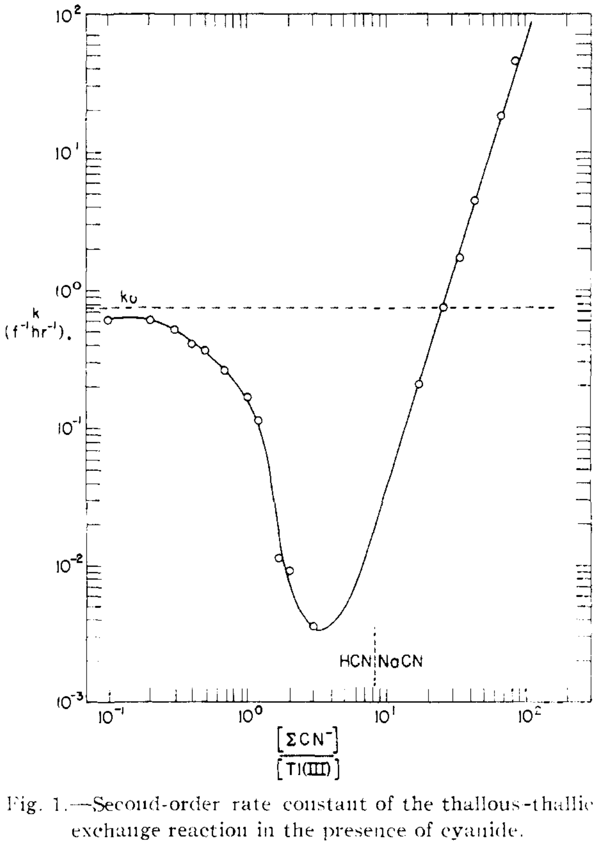

Fig. 1.—Second-order rate constant of the thallous-thallic exchange reaction in the presence of cyanide.

The exchange plots were straight lines, except in three runs as noted in Table I. In these runs, there was satisfactory linearity for about two half-lives, then the points tended to deviate above the curve. At the same time a brown discoloration developed in the solution. This was probably due to the formation of thallic hydroxide, to decomposition of the cyanide, or to both. In these runs the initial linear portion of the curve was used to estimate the half-time. The zero time exchange was between 3 and 7% in all runs.

We believe that the assignment of a standard deviation of 10% to the measured values of k is reasonable. Our value 0.74 f^{-1}-hr.$^{-1}$ for the rate constant in 0.50 f perchloric acid at 30° may be compared with the value 0.64 f^{-1}-hr.$^{-1}$ obtained in independent measurements.[6]

Since the rate of thallous–thallic exchange has been shown to be first order in the thallous and thallic concentrations under a wide variety of conditions,[4,5] the quantity $R/ab = k$ was calculated from the half-times and observed concentrations; this may be considered the second-order rate constant of the reaction, based on the thallium concentrations. The results of the measurements are given in Table I, and k is shown as a function of total cyanide concentration in Fig. 1. In most runs the cyanide was present essentially completely as HCN, since an excess of perchloric acid was present; in the last six runs, however, it was present largely as cyanide ion.

The data show that cyanide has a drastic effect on the rate of the reaction. A total variation of about 10,000-fold in k is observed. Small amounts diminish the rate; a minimum at less than 1% of the initial value of k is observed at a $(\Sigma CN^-)/(\Sigma Tl(III))$ ratio of 3.5; subsequently the rate rises about as the third power of (CN^-). A similar effect has been observed[6] with chloride in the Tl(I)–Tl(III) reaction, except that in this case the minimum occurs at a $(\Sigma Cl^-)/(\Sigma Tl(III))$ ratio of 1.5, is less deep, and the subsequent rise is a little less than second order in chloride.

We believe the decrease in rate caused by small amounts of cyanide can best be explained by the formation of thallium–cyanide complexes which are inert to the exchange reaction; indeed, no other plausible interpretation has occurred to us. On this view, the kinetic data furnish strong evidence for the existence of stable complexes $TlCN^{++}$ and $Tl(CN)^+$, and permit an estimate of the relative magnitude of the equilibrium constants for their formation. The initial effect is attributed to the formation of these species because: (1) there is evidence[16] for the existence of $Tl(CN)_4^-$ in aqueous solution; (2) stepwise association of Tl(III) with chloride and bromide, leading to very stable species, has been demonstrated[17]; (3) a self-consistent analysis of the data based on this assumption can be made, and (4) in general thallous ions forms only weakly associated complexes with simple anions.[18]

Consider the stepwise association reactions

$$A + X = AX. \text{ and } AX + X = AX_2$$

with the equilibrium constants

$$K_1 = \frac{(AX)}{(A)(X)} \text{ and } K_2 = \frac{(AX_2)}{(AX)(X)}$$

If K_1 and K_2 are each sufficiently large that the fraction of uncomplexed X is very small, mass balance leads to the expression

$$\frac{K_2}{K_1} = y\frac{\alpha - 1 + y}{(2 - \alpha - 2y)^2}$$

where α is the ratio of the formal concentration of X to that of A and y is the ratio of the concentration of uncomplexed A to the formal concentration of A. If one assumes that neither AX nor AX_2 react, and that higher complexes may be neglected for α less than 2, then $k/k_0 = y$, where k is the observed second-order rate constant, and k_0 is its value in the absence of the complexing agent X. Thus, the ratio of equilibrium constants can be calculated from the observed values of k. For the four runs in which α ranged from 0.7 to 1.7 the mean value of K_2/K_1 was found to be 0.15, with an average deviation of 0.05. The foregoing expression was solved for y, and evaluated at the values of α corresponding to the measurements in the range $0 < \alpha < 2$.

The concordance of the experimental data with this analysis is shown by the last column in Table I under the heading $k_{\text{predicted}}$. The average deviation between calculated and observed k's is 7% as k ranges from 0.735 to 0.011 mole^{-1} l. hr.$^{-1}$.

We ascribe the increase in rate at higher cyanide concentrations to the formation of other thallium-cyanide complexes. In view of the strong tendence of Tl(III) to complex with Cl^- and Br^-,[17] the generally strong complexing tendency of CN^-, and the fact that Tl(I) forms only weakly associated complex ions, it is most reasonable to infer that $Tl(CN)_3$ or $Tl(CN)_4^-$, reacting with Tl^+, are responsible for the increase near the minimum.

The continued subsequent increase may well be due to the equilibrium formation of still other thallium–cyanide species which participate more readily in the exchange reaction than the species which they replace. From analogy with the corresponding chloride system we are inclined to suppose that these are thallous complexes such as TlCN, $Tl(CN)_2^-$, or $Tl(CN)_3^{=}$. Equilibrium studies would aid in clarifying this point.

The acidity of the system would be expected to have a strong effect on equilibria involving cyanide and hence on the rates of reactions involving products of these equilibria. The hydrogen ion concentration would also appear in the rate expression if the reacting complex ions were themselves weak acids or the anions of weak acids, particularly if hydrogen atom transfer,[10,19] were important in the rate-determining step. That such effects occur is evident from the data in Table I, *e.g.*, in the results at total cyanide 0.193 and 0.200 *f*. The system in which cyanide was present largely as the free ion has a second-order rate constant at least 200 times greater than that in which it was present largely as HCN.

It would be of considerable interest to determine equilibrium constants for the formation of the various complexes of Tl(I) and Tl(III) with cyanide, and to relate these to the exchange kinetics. More extensive exchange measurements, at various temperatures and acidities, might then be profitably undertaken and the results related to the growing body of information about the rates of oxidation–reduction exchanges.

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The Polarographic Reduction of Ferric Ion in Fluoride Media

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West and Dean[1,2] have reported that the ferric ion in 1 *M* sodium fluoride exhibits no polarographic reduction wave to potentials as negative as *ca.* − 2 volts. Presumably, their medium would have a *p*H

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