the wave lengths of the absorption bands. The spectrum of the praseodymium system, as given in Fig. 1, is typical. Wave length values found were: La^{+3}, 5200, 5600, 6065 Å.; Pr^{+3}, 5220, 5600, 6050 Å.; Nd^{+3}, 5225, 5600, 6045 Å.; Sm^{+3}, 5220, 5600, 6040 Å.; Gd^{+3}, 5225, 5600, 6025 Å.; Y^{+3}, 5225, 5600, 6020 Å.; Er^{+3}, 5210, 5580, 6010 Å. All spectra amount to modifications of the naphthazarin spectrum produced by the presence of the rare earth metal ions.[3] In all cases, concentrations of these ions were too low to permit detections of any of the characteristic rare earth light absorptions.[5]

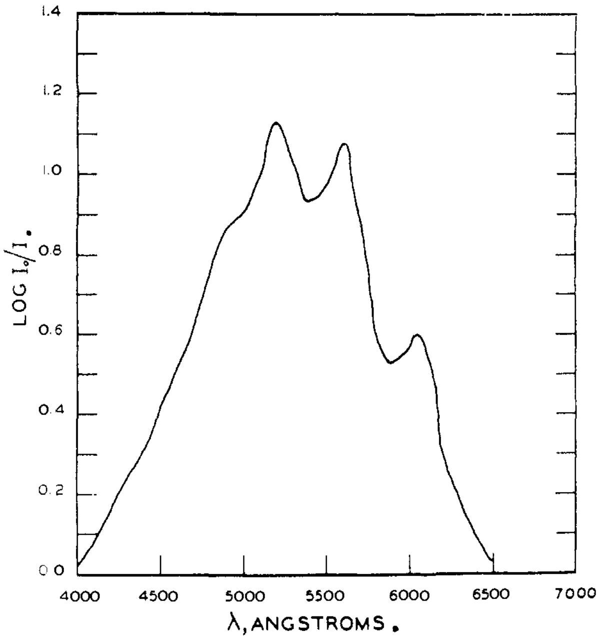

Fig. 1.– Absorption spectrum of praseodymium–naphthazarin complex in ethanol; concentration, 10.5 × 10^{-5} mole praseodymium per liter; measurements *ca.* 25°; Cary recording spectrophotometer with slit control at 10, chart range at 0–2.5, Hi-Lo Knob at Lo, gears at 60 driving, 60 driven, scanning at 5 Å. per sec.; 1.00 cm. demountable cells with quartz windows.

Compositions of the Colored Species.—Inasmuch as the absorption spectra of naphthazarin–praseodymium and naphthazarin–erbium solutions (taken as typical) showed no material variation, except in absorption intensities, for naphthazarin to rare earth metal ion mole ratios of 3:1, 2:1, 1:1, 1:2 and 1:3, the presence of but a single absorbing species was indicated in each instance. An application of a modification[6] of Job's method of continuous variations[7] to both praseodymium and erbium systems showed the colored species to contain naphthazarin and rare earth metal ions in 2:1 mole ratios. This is shown for praseodymium in Fig. 2.

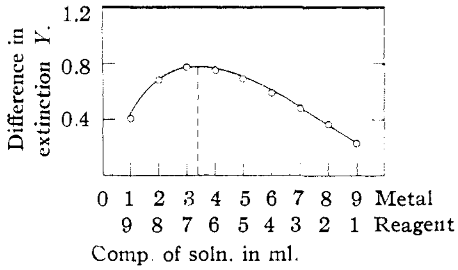

Fig. 2.– Continuous variations plot for praseodymium–naphthazarin system; measurements, *ca.* 25°; Cary recording spectrophotometer with slit control at 10, chart range at 0–2.5, Hi-Lo knob at Lo, gears at 60 driving 60 driven, scanning at 5 Å. per sec.; 1.00 cm. demountable cells with quartz windows.

Although this stoichiometry is the same as that of the thorium complex,[3] continuous variations data suggest the rare earth metal complexes to be somewhat less stable than the thorium species. As with thorium,[3] such species show cationic characteristics but have many of the properties of polymeric aggregates.

Adherence to Beer's Law.—As shown by the data in Table I, rather close adherence to Beer's law is obtained in praseodymium or erbium ion concentrations up to *ca.* 40 × 10^{-6} mole/liter. The marked similarities noted among the spectra of these systems irrespective of rare earth metal ion suggest adherence to Beer's law for the entire series.

TABLE I

BEER'S LAW ADHERENCE OF NAPHTHAZARIN–RARE EARTH METAL ION SYSTEMS

Metal ion concn., mole/l. × 10^6	Praseodymium, 6050 Å.		Erbium, 6010 Å.	
	k^a	$\epsilon^a \times 10^{-3}$	k	$\epsilon \times 10^{-3}$
7	68.96	9.71	65.75	11.00
14	72.00	10.13	62.35	10.43
21	69.97	9.86	67.90	11.33
28	70.48	9.93	70.15	11.72
35	67.74	9.54	70.90	11.86
42	65.92	9.29	68.40	11.43
49	63.45	9.35	65.65	10.98
56	62.11	8.75	63.03	10.54
Av.	67.58	9.57	66.77	11.16

[a] Specific extinction, k, is given by the relationship $k = (\log_{10} I_0/I)/cl$, l being in cm. and c being expressed in g. metal ion/l. When c is in mole/liter, k becomes ϵ, the molecular extinction.

Conclusions.—Although the naphthazarin reaction shows no specificity for individual rare earth metal ions, it is a sensitive color reaction for any member of the series.

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Burning Velocities of Isopropenyl and Diisopropenyl Acetylene

BY PAUL WAGNER

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The relationship between molecular structure and combustion behavior has been under investiga-

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(6) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

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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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[1] P. Wagner and G. L. Dugger, THIS JOURNAL, **77**, 227 (1955).

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

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RECEIVED JANUARY 5, 1955

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.