been evaluated for the system succinic dehydrogenase–succinate.

Slater and Bonner,[6] noting that fluoride and phosphate are competitive inhibitors of succinic dehydrogenase, determined the degree of inhibition obtaining under conditions in which the rate of the over-all reaction was varied by altering the concentration of the hydrogen acceptor, *i.e.*, methylene blue. In the course of their treatment, in which the symbols $e = [\mathrm{E}]$, $s = [\mathrm{S}]$, $v = -\mathrm{d}[\mathrm{S}]/\mathrm{d}t$ and $V = k_3'[\mathrm{E}]$ were employed, these authors arrived at the relation given in equation 3

$$V/v = 1 + (K_\mathrm{m}/s)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \tag{3}$$

where, in their symbolism, $K_\mathrm{m} = (k_2 + k_3')/k_1$, p and f the concentrations of phosphate and fluoride, and K_P, K_F and K_PF the respective enzyme–inhibitor dissociation constants. It was then argued that by expressing K_m in the form of its definition equation 3 may be transformed into equation 4

$$V/v = 1 + (k_2/k_1s)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) + (V/k_1se)(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \tag{4}$$

and that in the case in which V/v and v are the only variables, the relation given by equation 5 results by setting $V/v = 1$.

$$-V = k_2e \tag{5}$$

The constant k_1 was then evaluated from the relation $K_\mathrm{m} = (k_2 + k_3')/k_1$. That this practice is dubious is evident from the following considerations.

(a) The necessary condition for the derivation of equation 5 is that V/v assume a value of unity.

(b) When this condition is applied to equation 3 it is seen that it is required that either $s \rightarrow \infty$ or $K_\mathrm{m} = 0$ since the quantity $(1 + p/K_\mathrm{P} + f/K_\mathrm{F} + fp/K_\mathrm{P}K_\mathrm{PF}) \geq 1$.

(c) The condition is satisfactorily fulfilled when $s \rightarrow \infty$, this in fact being the definition of V, *i.e.*, $V = \lim\limits_{s \rightarrow \infty} v$.

(d) It is clear that the derivation of equation 5 by Slater and Bonner[6] is based upon setting $K_\mathrm{m} = 0$. In fact, the result itself is proof that this equality was assumed, since $V = k_3'e$ and hence $K_\mathrm{m} = (k_2 + k_3')/k_1 = 0$.

(e) The procedure used by Slater and Bonner[6] for the evaluation of k_1 is based upon the use of a value of k_2 obtained for the condition that $K_\mathrm{m} = 0$, *i.e.*, from equation 5, and the simultaneous use of values of K_m and k_3' for the system under conditions wherein $K_\mathrm{m} \neq 0$. It follows that the validity of a value of k_1 so obtained is entirely dependent upon a tacit assumed identity of the value of k_2 for the condition that $K_\mathrm{m} = 0$ with that for the condition that $K_\mathrm{m} \neq 0$. There is no reason to believe that such an extrapolation is necessarily valid.

Thus, even if it is granted that the system succinic dehydrogenase–succinate in the presence of fluoride and phosphate,[6] or of malonate,[7] can be described by equation 3 under the conditions employed by Slater and Bonner,[6] or by Thorn,[7] it is clear that this situation does not permit an unambiguous evaluation of k_1, k_2 or k_2/k_1 for the system succinic dehydrogenase–succinate.

The authors wish to express their indebtedness to Drs. R. Dilworth and R. J. Foster for their counsel.

CONTRIBUTION NO. 1946 FROM THE
GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIFORNIA

Observations on the Rare Earths. LXV. Naphthazarin Complexes of Certain Rare Earth Metal Ions

BY THERALD MOELLER AND MELVIN TECOTZKY

RECEIVED NOVEMBER 26, 1954

A phase of rare earth metal chemistry which has received only limited attention is that of colored complexes formed with various organic reagents. In this connection, an early observation by Formánek[1] on the formation of red-violet to blue colors by reaction of the dye alkannet with thorium and rare earth metal ions is of interest. Major light absorptions in the wave length region 6120–6010 Å., with minor absorptions in the regions 5662–5559 Å. and 5262–5177 Å., were reported, with wave lengths decreasing in the series lanthanum to erbium. More recently, attention has been refocused upon this type of reaction by the development of a spectrophotometric beryllium determination using either alkannin or its unsubstituted parent, naphthazarin (5,8-dihydroxy-1,4-naphthoquinone),[2] and naphthazarin has been applied to the micro-determination of thorium.[3] Since in the determination of thorium interferences are caused by the rare earth metal ions, it has been of interest to study reactions of these species with naphthazarin. Spectrophotometric studies on such reactions and evaluations of the compositions of the colored complexes obtained are reported here.

Experimental

Materials.—Rare earth metal ions were used as 0.0021 *M* chloride stock solutions prepared from 98% to atomic weight purity oxides from the University of Illinois stocks. Naphthazarin was prepared and purified by the method of Toribara and Underwood.[4] It was used as 0.0021 *M* solution in absolute ethanol.

Absorption Spectra.—All absorption spectra were determined at *ca.* 25° with either a Beckman Model DU quartz spectrophotometer or a Cary Recording Spectrophotometer, using 1.00 cm. quartz cells with the former and 1.00 cm. demountable cells with quartz windows with the latter.

Color Reactions.—The colored complexes were obtained in solution merely by mixing the aqueous rare earth metal chloride solutions and the ethanolic naphthazarin solutions. Visible color changes resulted at concentrations as low as 0.31 mg. of rare earth metal ion per ml. In every instance, the red color of the naphthazarin was replaced by the reddish-blue of the complex. For absorption spectra measurements, solutions prepared from 5 ml. of the salt solution and 10 ml. of the naphthazarin solution and diluted to 100 ml. with absolute ethanol were found convenient.

Results and Discussion

Absorption Spectra.—Spectra obtained from solutions containing lanthanum, praseodymium, neodymium, samarium, gadolinium, erbium and yttrium ions were all essentially similar except in

---

(1) J. Formánek, *Z. anal. Chem.*, **39**, 673 (1900).

(2) A. L. Underwood and W. F. Neuman, *Anal. Chem.*, **21**, 1345 (1949).

(3) T. Moeller and M. Tecotzky, *ibid.*, **27**, in press (1955).

(4) T. Y. Toribara and A. L. Underwood, *ibid.*, **21**, 1352 (1949).

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]

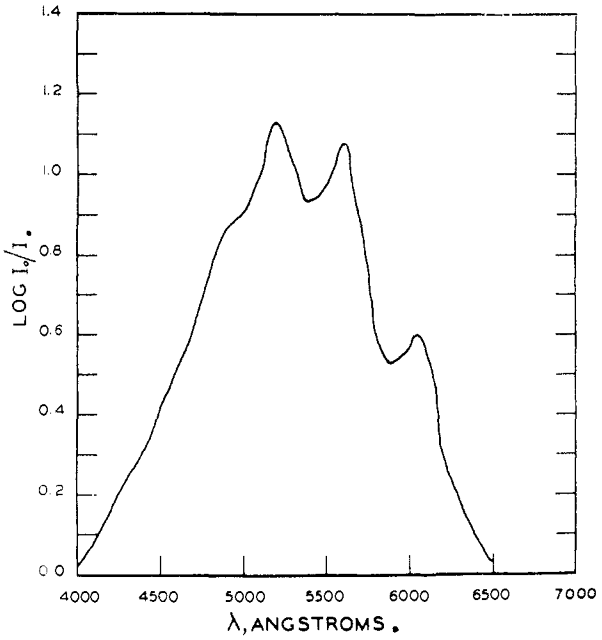

Fig. 1.– Absorption spectrum of praseodymium–naphthazarin complex in ethanol; concentration, 10.5 × 10^{-5} mole praseodymium per liter; measurements *ca.* 25°; Cary recording spectrophotometer with slit control at 10, chart range at 0–2.5, Hi-Lo Knob at Lo, gears at 60 driving, 60 driven, scanning at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

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.

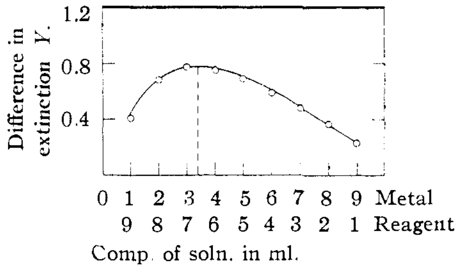

Fig. 2.– Continuous variations plot for praseodymium–naphthazarin system; measurements, *ca.* 25°; Cary recording spectrophotometer with slit control at 10, chart range at 0–2.5, Hi-Lo knob at Lo, gears at 60 driving 60 driven, scanning at 5 Å. per sec.; 1.00 cm. demountable cells with quartz windows.

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.

Acknowledgment.—Support received from an E. I. du Pont de Nemours and Co. Grant-in-aid is gratefully acknowledged.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Burning Velocities of Isopropenyl and Diisopropenyl Acetylene

BY PAUL WAGNER

RECEIVED DECEMBER 3, 1954

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

---

(5) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

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

(7) P. Job, *Ann. chim.*, [10] **9**, 113 (1928).