[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Chemistry of Thorium. V. Some Observations on the 8-Quinolinol Chelates of Thorium

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Thorium forms with 8-quinolinol a yellow chelate of composition $Th(C_9H_6NO)_4$ and an orange compound of composition $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$. The latter compound is obtained reproducibly by precipitation at *p*H 4.3 and drying at not above 80–85° and has a lower thermal stability than commonly reported. Absorption spectra and X-ray diffraction data indicate that although the 1 to 5-compound is a chemical entity, it has a stable existence only in the solid state. It is suggested that the extra mole of 8-quinolinol is held, therefore, by weak lattice forces. The 1 to 4- and 1 to 5-compounds give absorption spectra differing only in absorption intensities in a variety of organic solvents. For all solvents except absolute ethanol, these spectra suggest hydrolytic decompositions to 8-quinolinol. For absolute ethanol, the spectra compared with those of stable inner complex 8-quinolinol chelates but are converted by the addition of water to the spectrum of 8-quinolinol. The 8-quinolinol derivatives of thorium are of no use for the spectrophotometric determination of that element.

Introduction

Thorium(IV) might be expected, logically, to form an 8-quinolinol chelate in the 1 to 4 stoichiometry represented by the formula $Th(C_9H_6NO)_4$. Hecht and Reich-Rohrwig[1] reported the preparation of what appeared to be the 1-hydrate of such a compound. The material lost weight rapidly at 160–170° to a constant value, the dried residue then having the expected composition of an anhydrous 1 to 4-compound, as shown by bromination analysis. Unheated samples, however, gave high results upon bromination, although this difficulty was said to be avoided by washing with 25% ethanol. The inconsistencies in these results were resolved by Frere,[2] who showed conclusively that precipitation from an acetate buffer yields an orange compound of the 1 to 5 stoichiometry, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$. This compound was reported to be reasonably stable up to 100–110° but to decompose to the yellow 1 to 4-compound at 160–170° and then to undergo further decomposition on further heating. In contact with 8-quinolinol solutions, the yellow material reverted to the orange. Hecht and Ehrmann[3] confirmed the formation of the 1 to 5-compound and suggested its use for the determination of thorium.

Although the formation of two 8-quinolinol chelates of thorium is well established, the temperature ranges for stability appear to be in some question. Berg[4] indicates loss of the extra mole of 8-quinolinol at 150–160°. Thermogravimetric analysis of the orange compound, however, indicates no weight loss to a constant composition in the range 20–945°.[5] Borrell and Pâris,[6] using the same experimental technique, find, to the contrary, that the anhydrous orange 1 to 5-compound is stable only to *ca.* 80°, decomposition by an intermolecular dehydration mechanism occurring above 136° and the 1 to 4-compound resulting only at 245°. Further decompositions result above 345°.

The inconsistencies among these data indicate clearly the need for further studies both on the reproducible preparation of the 1 to 5-chelate in a state of purity and upon the region of stability of this compound. To this end, precipitation under conditions of accurate *p*H control *via* the controlled thermal decomposition of urea has proved particularly valuable. It has been of interest to consider also the nature of the bonding in the unusual 1 to 5-compound. For this purpose, absorption spectra and X-ray diffraction measurements have been used. The successful applications of many 8-quinolinol chelates in colorimetric determinations[7-9] have prompted extension of absorption studies and investigation of extraction techniques from the analytical point of view.

Experimental

Materials Used.—The source of thorium ion was a sample of thorium nitrate 4-hydrate, obtained from the Lindsay Chemical Company and shown to be free from yttrium and the rare earth elements. The 8-quinolinol used was an Eastman Kodak Co. product which had been resublimed. Chloroform employed contained *ca.* 1% ethanol by volume as preservative. All other chemicals were of analytical reagent quality.

Thorium nitrate solutions were standardized gravimetrically by weighing as the oxide. 8-Quinolinol was used in acetic acid solution.

Preparation of 8-Quinolinol Chelates.—For the preparation of the 1 to 5-chelate, numerous experiments were carried out in which conditions for precipitation and for drying the product were altered. Each preparation involved a known quantity of thorium ion and was followed by weighing the dried product and analyzing for 8-quinolinol either by bromination, by loss in weight upon ignition, or by micro carbon, hydrogen and nitrogen determinations. Results obtained by bromination were erratic and generally unreliable. Ignition to thorium dioxide ran more smoothly when carried out in the presence of oxalic acid. The following procedure gives products of consistent properties: Two hundred ml. of thorium nitrate solution (5.49 mg. Th/ml.) is diluted to 1800 ml. and treated with 400 ml. of 8-quinolinol solution (25 g. of reagent and 50 ml. of glacial acetic acid in 1000 ml. total volume) and 80 g. of urea. The suspension is heated on the steam-bath for 5 hr. (final *p*H 4.3). After 12 hr. standing at room temperature, the precipitate is removed, washed with cold water, dried in air, powdered and dried for 30 min. at 80–85°. *Anal.* Calcd. for $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$: C, 55.66; H, 2.28; N, 7.34; 8-quinolinol, 75.67. Found: C, 55.87, 55.77; H, 3.56; N, 7.33, 7.30; 8-quinolinol, 75.90, 75.90.

Conversion of this product to the 1 to 4-chelate is effected by heating at 120–125° for 5 hours and then at 130–135° for 1 hour. *Anal.* Calcd. for $Th(C_9H_6NO)_4$: C, 53.46; H, 2.99; N, 6.92; 8-quinolinol, 71.30. Found: C, 53.20; H, 2.89; N, 7.07; 8-quinolinol, 71.20.

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[1] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, *Wegscheider Festschrift*, **53-54**, 596 (1929).

[2] F. J. Frere, THIS JOURNAL, **55**, 4362 (1933).

[3] F. Hecht and W. Ehrmann, *Z. anal. Chem.*, **100**, 98 (1935).

[4] R. Berg, "Die Chemische Analyses, Vol. XXXIV. Das o-Oxychinolin, 'Oxine,'" Ferdinand Enke, Stuttgart, 1935, p. 60.

[5] T. Dupuis and C. Duval, *Anal. Chim. Acta*, **3**, 589 (1949).

[6] M. Borrell and R. Pâris, *ibid.*, **4**, 267 (1950).

[7] T. Moeller, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 270, 346 (1943).

[8] T. Moeller and A. J. Cohen, *Anal. Chem.*, **22**, 686 (1950).

[9] T. Moeller and A. J. Cohen, THIS JOURNAL, **72**, 3546 (1950).

Absorption Spectra Measurements.—All absorption spectra were measured with either a Beckman model DU quartz spectrophotometer or a Cary Recording Spectrophotometer, using 5.0-cm. demountable cells with quartz windows.

X-Ray Diffraction Measurements.—All measurements were made with Cu-K$_\alpha$ radiation at 40 kv. and 15 ma., using an exposure time of 7 hours.

Results and Discussion

Preparation of 8-Quinolinol Chelates.—Optimum conditions for the preparation of the 1 to 5-compound involve slow precipitation with *ca.* three times the equivalent quantity of 8-quinolinol at *p*H 4.3, washing with water, and drying for not more than 30 min. at not above 85°. Under these conditions, the pure compound is obtained in stable form. Conversion to the 1 to 4-chelate begins above 85° but is slow below 120–135°. It will be noted that the conversion proceeds at lower temperature than has been generally reported. At room temperatures, both compounds appear to be stable indefinitely.

Absorption Spectra Studies.—The 8-quinolinol chelates of thorium, like those of many other metals, are soluble in organic solvents such as chloroform, acetone, carbon tetrachloride, methanol, ethanol, butanol and benzene. The orange compound dissolves more readily than the yellow one, and both are more soluble in chloroform than in the other solvents mentioned. All solutions in these solvents are only pale yellow in color, in contrast with the intensely yellow solutions produced for example, by the aluminum family 8-quinolinol chelates.[9]

As indicated in Fig. 1, the absorption spectra of both the orange 1 to 5-compound and the yellow 1 to 4-compound in chloroform are similar in that major absorption occurs at 3200 Å., with perhaps an indication of absorption at *ca.* 3720 Å. That neither of these bands obeys Beer's law is apparent from the data summarized in Table I. It is apparent also from both Fig. 1 and Table I that addition of an equivalent quantity of 8-quinolinol to a chloroform solution of the 1 to 4-chelate gives an absorption spectrum nearly identical with that of the 1 to 5-chelate, suggesting strongly that upon dissolution the extra mole of bonded 8-quinolinol is lost.

Table I

Absorption Spectra Data for Chloroform Solutions

Chelate	Concn., mg. Th/l.	log I_0/I		Specific extinction[a]	
		3200 Å.	3720 Å.	3200 Å.	3720 Å.
$Th(C_9H_6NO)_4$	6.0	0.99	0.45	33.00	15.00
	5.0	.86	.31	34.40	12.40
	4.0	.73	.20	36.50	10.00
	3.0	.56	.11	37.30	7.30
	2.0	.39	.05	39.00	5.00
	1.0	.20	.01	40.00	2.00
$Th(C_9H_6NO)_4 \cdot C_9H_6NOH$	6.0	1.20	0.45	40.00	15.00
	5.0	1.05	.34	42.00	13.60
	4.0	0.87	.23	43.50	11.50
	3.0	.68	.14	45.30	9.30
	2.0	.47	.07	47.00	7.00
	1.0	.23	.02	46.00	4.00
$Th(C_9H_6NO)_4 + C_9H_6NOH$	6.0	1.25	0.32	41.60	10.10
	5.0	1.11	.23	44.40	9.20
	4.0	0.94	.15	47.00	7.50
	3.0	.72	.09	48.00	6.00
	2.0	.50	.04	50.00	4.00
	1.0	.25	.01	50.00	2.00

[a] Specific extinction, k, is given by the relation $k = (\log I_0/I)/cl$, l being in cm. and c being expressed as g. Th/liter.

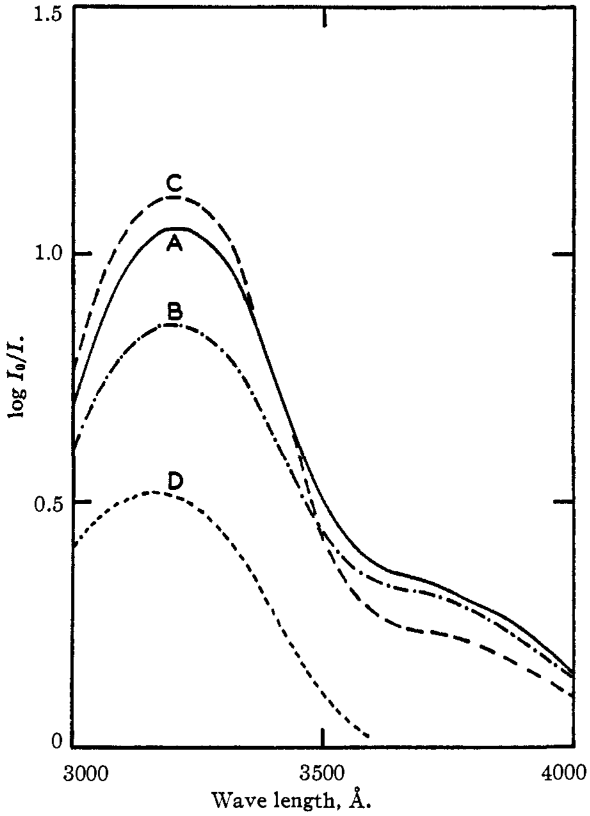

Fig. 1.—Absorption spectra of chloroform solutions: A, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, 5 mg. Th/l.; B, $Th(C_9H_6NO)_4$, 5 mg. Th/l.; C, $Th(C_9H_6NO)_4$ and C_9H_6NOH, 5 mg. Th/l., D, C_9H_6NOH, 6.2 mg./l.

The absorption spectra given in Fig. 1 are markedly like those of aluminum family chelates which have undergone photochemical decomposition.[9,10] However, a comparative study using chloroform solutions of the 1 to 5-compound showed that although exposure to bright light for 72 hr. increased the intensity of absorption at 3200 Å. while decreasing that at 3720 Å., the effects were too slight to suggest that the magnitude of the effect shown in Fig. 1 could be due to photochemical action alone. Nor is this entirely a temperature effect, absorption data at below 10° being essentially identical with those at 25°. Regardless of decomposition mechanism, however, the similarities between these spectra and that of 8-quinolinol (Fig. 1) indicate clearly that the latter material is a decomposition product.

With the thought that the decomposition might be a function of the solvent, absorption spectra were measured using a variety of solvents. Representative data for the 1 to 5-compound, as given in Fig. 2, show the effect to be common to all the solvents studied except absolute ethanol. With this medium, spectra comparable with those considered to be characteristic of undecomposed 8-quinolinol

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(10) A. J. Cohen, Doctoral Dissertation, University of Illinois (1949).

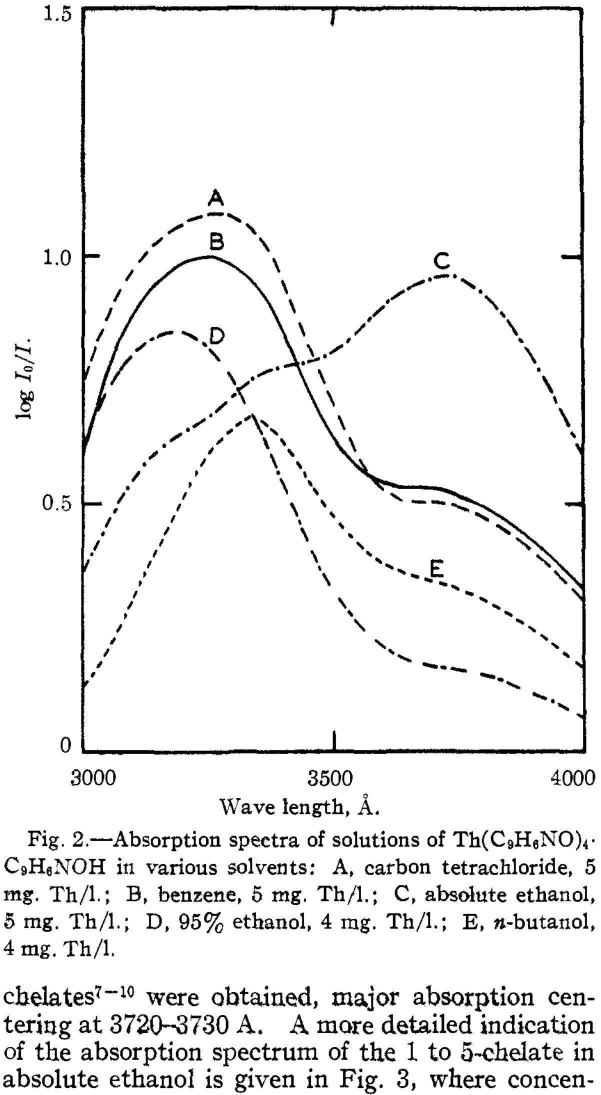

Fig. 2.—Absorption spectra of solutions of $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$ in various solvents: A, carbon tetrachloride, 5 mg. Th/l.; B, benzene, 5 mg. Th/l.; C, absolute ethanol, 5 mg. Th/l.; D, 95% ethanol, 4 mg. Th/l.; E, *n*-butanol, 4 mg. Th/l.

chelates[7-10] were obtained, major absorption centering at 3720–3730 A. A more detailed indication of the absorption spectrum of the 1 to 5-chelate in absolute ethanol is given in Fig. 3, where concentration effects are shown. Solutions of the 1 to 4-compound in absolute ethanol gave the same type of spectra, but with decreased extinction values. As shown by the data in Table II, however, strict adherence to Beer's law is not observed.

TABLE II

ABSORPTION SPECTRA DATA FOR ABSOLUTE ETHANOL SOLUTIONS OF $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$

Concn., mg. Th/l.	log I_0/I 3330 Å.	log I_0/I 3720 Å.	Specific extinction 3330 Å.	Specific extinction 3720 Å.
5.0	0.83	1.15	33.20	46.00
4.0	.67	0.93	33.50	46.50
3.0	.51	.67	34.00	44.67
2.0	.34	.45	34.00	45.00
1.0	.18	.21	36.00	42.00

The differences between the spectra in absolute and 95% ethanol suggest strongly that the decomposition is due to water and is hydrolytic in character. The effect of water in altering the spectrum in absolute ethanol, as shown in Fig. 3, together with the previously mentioned similarity between the spectra of the decomposed solutions and that of 8-quinolinol support this hypothesis and indicate the formation of the latter as a decomposition product. The fact that consideration of the observed 3200 Å. absorption band as being due to 8-quinolinol and estimation of the 8-quinolinol content of the solution from the intensity of this band never gives quite the quantity of that material expected for complete decomposition suggests that the process is essentially an equilibrium one. It is of interest, however, that rigorous drying of chloroform and benzene with phosphorus(V) oxide and sodium hydride, respectively, does not alter the spectra of the 1 to 5-compound in these media. If water is indeed the only factor, then it must be effective in very small quantities. Perhaps the tolerance of ethanol for larger quantities of water is due to a sort of protective coördination of ethanol to the dissolved complex.

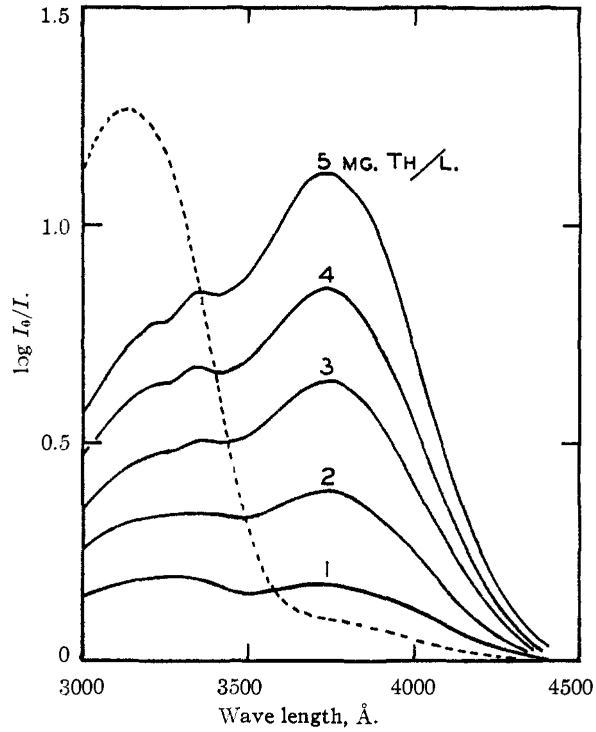

Fig. 3.—Absorption spectra of solutions of $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$ in absolute ethanol: dotted curve, 5 mg. Th/l. in solution containing 20% water by volume.

Analytical Aspects of the Thorium Chelates.—The low absorption intensities and the lack of adherence of solutions of the chelates to Beer's law indicate clearly the lack of utility of the thorium chelates for spectrophotometric determinations. Although thorium is apparently extracted into the non-aqueous phase in the presence of 8-quinolinol at *p*H values around 4.9 and above, the absorption spectra of the extracts are those of 8-quinolinol. When run against an 8-quinolinol solution as blank, absorptions at *ca.* 3750 Å. are noted, but they are not in accord with Beer's law. These compounds appear to be useless for the colorimetric determination of thorium.

X-Ray Diffraction Studies.—Interplanar spacings determined for both the 1 to 5- and the 1 to 4-compounds, as summarized in Table III, indicate that in the solid state these compounds are definitely different from each other. Comparison of these values with those for 8-quinolinol and for an

TABLE III

INTERPLANAR(d) SPACINGS

$Th(C_9H_6NO)_4$, Å.	$Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, Å.	$Th(C_9H_6NO)_4 + C_9H_6NOH$, Å.	C_9H_6NOH, Å.
9.82[a]	10.60[a]	9.65[a]	9.74[a]
7.89[a]	8.38[a]	7.78[a]	7.31
7.02[a]	7.31[a]	6.97[a]	6.33[a]
4.34[a]	6.56	4.34[a]	5.82
4.02	6.01	4.04	3.83[a]
3.57	5.42	3.55	3.50[a]
3.27	4.68	3.27	3.32
3.07[a]	4.23[a]	3.07[a]	3.19[a]
2.90	3.71[a]	2.91	3.03
2.71	3.00	2.69	2.91
2.43	2.12	2.43	2.80
2.33		2.34	2.46
2.16		2.16	2.39
			1.92
			1.79

[a] Major spacings.

equimolar mixture of the 1 to 4-compound and 8-quinolinol indicate further that in the 1 to 5-material chemical union involving the extra 8-quinolinol must occur rather than any simple physical mixing.

Natures of the Thorium Chelates.—The 1 to 4-compound $Th(C_9H_6NO)_4$, appears to be a normal chelate in which thorium is exhibiting a coördination number of eight. The 1 to 5-compound, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$, is a different species but, as shown by absorption spectra measurements, it possesses this identity only in the solid state and becomes indistinguishable from the 1 to 4-material in solution. The stability of the solid is then due to the very loosely bound 8-quinolinol. It seems very probable that this additional molecule of 8-quinolinol is then only a component of the crystal lattice and is held by weak lattice forces. In this respect the thorium compound is strictly comparable with the analogous 8-quinolinol derivative of scandium.[11]

Acknowledgment.—Funds received from an E. I. du Pont de Nemours and Company Grant-in-Aid for partial support of this investigation are gratefully acknowledged.

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[11] L. Pokras, M. Kilpatrick and P. M. Bernays, THIS JOURNAL, **75**, 1254 (1953).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Salt Effects and Chelation in the Decomposition of Diazomalonic Acid[1]

BY CECIL V. KING AND IRWIN A. LICHTMAN

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The decomposition of diazomalonic acid in dilute aqueous solutions is subject to general base catalysis. When an attempt was made to detect catalysis by cation bases like the pentaaquohydroxy aluminum ion, and for comparison to study salt effects in dilute acid or buffer solutions with the trivalent lanthanum and cerium ions, highly abnormal results were obtained. The reason was traced to the formation of chelates between these ions and the diazomalonate ion, resulting in a complete change in the mechanism of decomposition. The chelate ions have the general formula $M(N_2C(COO)_2)_2^-$.

It was shown previously[2,3] that diazomalonate ion reacts in dilute strong acid or in acidic buffers according to the equation

$$N_2C(COO)_2^{=} + H_3O^+ \longrightarrow N_2 + CO_2 + CH_2OHCOO^- \quad (1)$$

The reaction is subject to general base catalysis, and the acid intermediate ion also reacts in a similar manner. The rate equation contains two terms for water catalysis and two terms for each additional base present

$$dx/dt = k_1C_{N^=} + k_2C_{HN^-} + k_3C_AC_{N^=} + k_4C_AC_{HN^-} \quad (2)$$

Here $N^=$ and HN^- represent the two diazo ions, and A is any other basic species than water. Terms in C_{HN^-} are negligible at *p*H above 4, and at sufficiently low acidity base catalysis is not evident, the rate being controlled by the hydrogen ion concentration.

The present work started with an attempt to detect general base catalysis in the decomposition of the diazomalonic ethyl ester ion $N_2C(COOC_2H_5)(COO)^-$, which decomposes in a similar manner in dilute strong acid.[2] The results with acetate ion were inconclusive, and as a possible catalyst aluminum chloride was added to an acetate buffer; cation bases like $Al(H_2O)_5(OH)^{++}$ have been found very effective catalysts in certain cases.[4] The rate was increased somewhat. To compare with normal salt effect, lanthanum chloride was chosen as an inert, unhydrolyzed salt of the same valence type; it has often been used for similar purposes.[5] This salt made the rate extremely low.

Since rates with the ester-ion were inconveniently low and further studies did not appear promising, experiments were continued with the dipotassium diazomalonate to see if cation base catalysis could be detected, and if salt effects with trivalent metal ions could be studied.

Experimental

Rate Measurements.—Rates were determined by the gas pressure method as described before,[2] at 25 ± 0.02°. In all experiments reported, the first-order law could be used to calculate rate constants, and the Guggenheim method was ordinarily employed. Actually, in certain solutions used, the first-order constant varied several per cent. with the initial diazomalonate concentration, probably because of changes in total ion concentration, but this is of mino

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[1] Based on a Ph.D. thesis submitted by Irwin A. Lichtman to the Graduate School of New York University, February, 1953.

[2] C. V. King, P. Kulka and A. Mebane, THIS JOURNAL, **72**, 1906 (1950).

[3] C. V. King and P. Kulka, *ibid.*, **74**, 3128 (1952).

[4] J. N. Brönsted and K. Volquartz, *Z. physik. Chem.*, **A155** 211 (1931).

[5] V. K. LaMer and R. W. Fessenden, THIS JOURNAL, **54**, 2351 (1932).