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.

[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

RECEIVED APRIL 21, 1953

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).

importance. Observed rate constants are labeled k' as before.

Materials.—The potassium diazomalonate was the sesquihydrate and was about 95% pure, as deduced from the amount of acid disappearing during its decomposition.[3] Ordinarily a sample of 87.5 mg. was employed, with 50 ml. of solution, and the original concentration is called 0.0075 *M*.

Sodium and barium chlorides, acetic acid and sodium acetate were of analytical grade. Lanthanum chloride ($7H_2O$) was a commercial C.P. product; cerium(III) chloride ($7H_2O$) was from G. Frederick Smith; aluminum chloride ($6H_2O$) was a Merck Reagent salt. The salts were used without further purification after it was shown that stock solutions contained within 1-2% of the proper amount of chloride, and that lanthanum chloride, recrystallized with hydrogen chloride[6] and dried at 120°, gave identical results.

Although the first work with diazomalonate was done with perchloric acid, there has been no evidence that hydrogen chloride replaces nitrogen. Consequently the chlorides were used in the present work.

Salt Effects.—Figure 1 shows the effect of additions of sodium, barium, lanthanum and cerium(III) chlorides to an acetate buffer. The rate in the buffer alone is in accord with the value found before.[2] The constant k' consists of the sum of values for the rate-controlling steps

$$\begin{aligned} N^= + H_2O &\longrightarrow \text{complex}_1 \quad k_1 = 0.014 \\ N^= + Ac^- &\longrightarrow \text{complex}_3 \quad k_3 = 0.042 \end{aligned} \tag{3}$$

The effects of sodium and barium chlorides are mainly primary salt effect on the second reaction, but the effect of the first salt seems quantitatively too small, of the second probably too large.

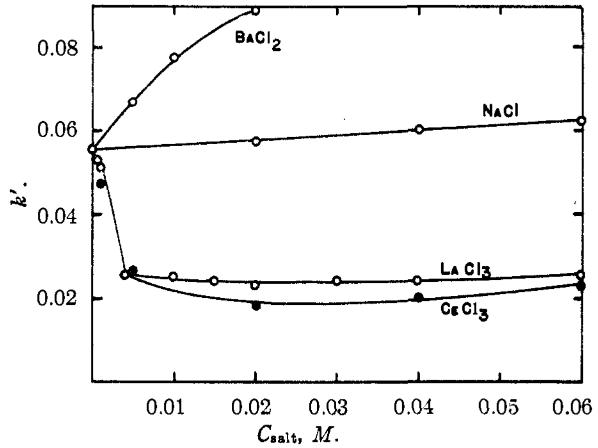

Fig. 1.—The effect of salts on the rate in a buffer containing 0.05 *M* acetic acid, 0.05 *M* sodium acetate, at 25°.

The main interest is in the trivalent metal ions, whose role is obviously not that of exerting a simple salt effect. Aluminum chloride, in solutions above 0.005 *M*, reduces the rate practically to zero; there is no suggestion of cation base catalysis. The fact that lanthanum and cerium ions have little further effect beyond 0.004 or 0.005 *M*, suggests that these ions form complexes which are more stable in this buffer than the simple diazo ion. Since the existence of such complexes has been proved independently, as described later, it will be assumed in the following paragraphs.

In acetic acid alone the decomposition rate is smaller than in buffers; it is due to water catalysis alone, and is independent of the acid concentration. Lanthanum chloride increases the rate remarkably, as shown in Fig. 2. At least two effects must be assumed: (a) the complex is formed and reacts directly with hydrogen ion, molecular acetic acid, or both; (b) excess lanthanum ion increases the ionization of acetic acid and thus provides more hydrogen ion (secondary salt effect).

In contrast, aluminum chloride depresses the rate in 0.025 *M* acetic acid practically to zero.

With fixed concentrations of lanthanum or cerous chloride, with or without added sodium acetate, increasing acetic acid concentration leads to a large increase in rate, as shown in Fig. 3. If most of the rate were due to reaction of the complex with hydrogen ion, there should be greater differences between curves A and B, also between B and C of Fig. 3. While addition of acetate ion decreases the rate, the 35-fold change in hydrogen ion concentration of Fig. 4 is accompanied by only a 2.3-fold change in decomposition rate. These facts suggest that a large portion of the decomposition consists in reaction of the complex with (or catalysis by) molecular acetic acid.

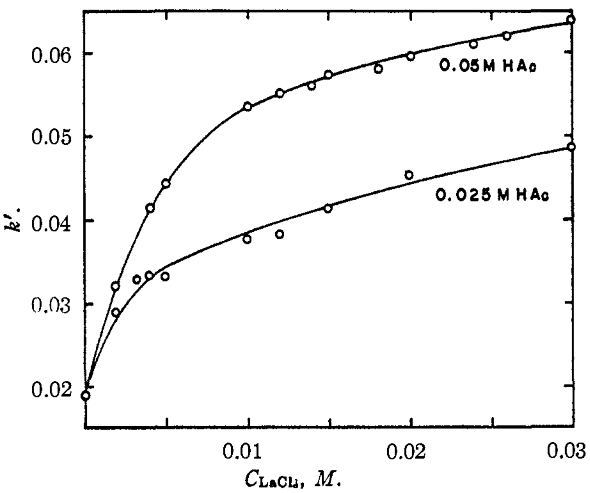

Fig. 2.—The effect of lanthanum chloride on the rate in dilute acetic acid alone, at 25°.

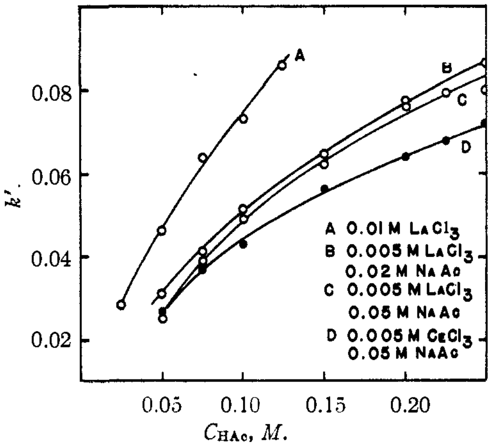

Fig. 3.—The effect of increasing acetic acid concentration, with fixed concentration of lanthanum or cerium(III) chlorides.

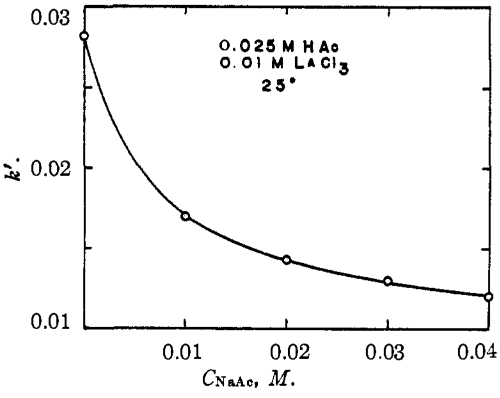

Fig. 4.—The effect of sodium acetate, with fixed acetic acid and lanthanum chloride concentrations.

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[6] C. M. Mason, This Journal, 60, 1638 (1938).

Figure 5 shows the complicated effect of lanthanum chloride in two buffers of nearly the same *p*H (about 4.3). There is, in each buffer, an initial increase in rate due to formation of the complex. This is followed by a decrease, which is probably a primary salt effect if part of the reaction is that of hydrogen ion with a negative complex ion. The increase at still higher lanthanum ion concentrations may be due to secondary salt effect. The large difference in rates in solutions of nearly the same *p*H, since it is not due to the different acetate ion concentrations, again suggests reaction with molecular acetic acid.

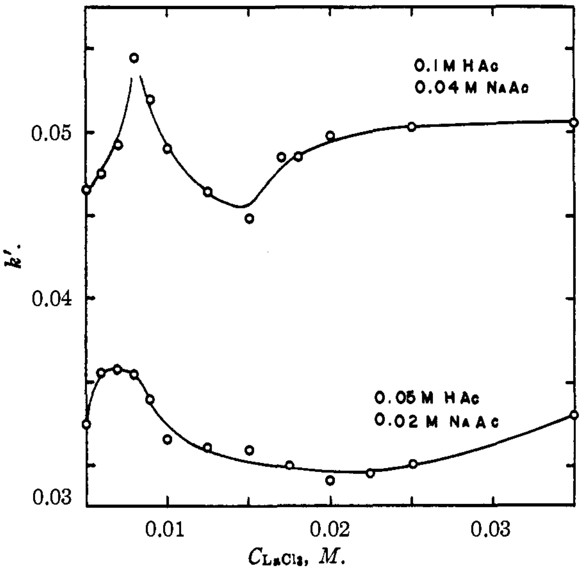

Fig. 5.—The effect of lanthanum chloride in two buffers of the same *p*H, at 25°.

Since lanthanum ion increases the rate in solutions of lower *p*H, experiments were run in dilute perchloric acid, as shown in Fig. 6. The increase in rate up to about 0.004 *M* lanthanum ion is no doubt due to formation of the complex. Above that concentration the further increase is not a normal salt effect if the complex ion has a negative charge. As will be shown below, these complexes, or chelates, are somewhat dissociated, and part of the effect of excess lanthanum ion is to repress this dissociation, since the complex is more reactive than the simple diazomalonate ion.

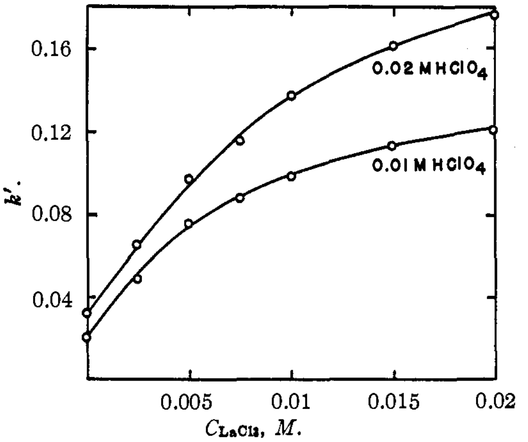

Fig. 6.—The effect of lanthanum chloride on the rate in dilute perchloric acid, at 25°.

Addition of aluminum chloride again results in stabilizing the diazomalonate, as shown in Table I. Evidently the low concentrations, 0.001 and 0.002 *M* aluminum ion are insufficient to convert all the diazomalonate (0.0075 *M* at the start of the reaction) into the non-reactive chelate, while 0.005 *M* is enough to do so.

Table I also gives the results of a few experiments with violet and green chromic chloride solutions, containing principally the ions $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_4Cl_2^+$, respectively. Evidently these chromic ions do not form chelates with diazomalonate ion as the other trivalent metals do.

TABLE I

THE EFFECT OF ALUMINUM AND CHROMIC CHLORIDES ON THE RATE IN 0.02 *M* $HClO_4$, AT 25°

C_{AlCl_3}, *M*	k'	C_{CrCl_3}, *M*	k
0	0.032	Violet	
0.001	.028	0.02	0.031
.002	.027	.04	.030
.005	[a]	Green	
.01	[a]	.02	.035
.02	[a]	.04	.039
.04	[a]		

[a] Very slow, incomplete in three days.

Study of the Chelates.—Since complexes between the metal ions and the diazomalonate are most likely chelate in nature, we shall assume that they are. Malonic acid and its derivatives form chelates with many metal ions,[7] and many bi- and tridentate chelating agents form complexes with rare earth and aluminum ions.

When diazomalonate samples were introduced into the less acid solutions containing lanthanum chloride, the solutions occasionally became slightly cloudy. When more concentrated, neutral solutions were mixed, a white, almost colloidal precipitate was obtained, small amounts of which dissolved easily in dilute acids. The solid settled slowly, became sticky or tacky, and was difficult to filter or wash. Attempts to isolate and dry the compound resulted only in a brown decomposition product (mainly lanthanum oxide).

The composition of the chelates was determined by means of conductance titrations as shown in Fig. 7. A number of titrations were carried out both at 25 and at 0°. The aluminum chelate is the most stable, but reasonably good end-points are obtained with the other metals. Molar ratios obtained were La^{+++}:$N^=$, 1:1.91, 1:2.14; Ce^{+++}:$N^=$, 1:2.01, 1:2.08; Al^{+++}:$N^=$, 1:2.00. Since the diazomalonate was about 95% pure (which was not considered in calculating the above ratios), we can confidently assume the formulas MN_2^-. No evidence of chelates of other molar ratio was found. Since barium chloride seemed to have an unusually large salt effect (Fig. 1), a similar titration of diazomalonate with 0.1 *M* barium chloride was carried out, but only a normal conductance curve for the salt mixture was obtained. There was some question as to whether acetate ion might not coördinate with lanthanum ion, but a conductance titration showed that this is not the case.

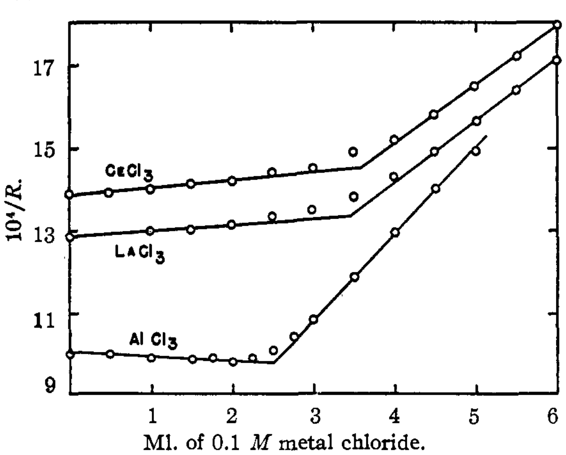

Fig. 7.—Conductance titrations at 0°: Al curve, 0.5 millimole diazomalonate in 60 ml. water; the others, 0.75 millimole diazomalonate in 65 ml. water. The curve for Ce is shifted upward one unit.

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(7) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 514.

Titration of malonic acid and sodium malonate with lanthanum and aluminum chlorides gave no indication of chelate formation. Malonic acid chelates with bivalent metal ions are reported in the literature.

Ultraviolet absorption studies can give some information regarding the chelates, though it was found impossible to deduce their composition from such measurements. The absorption studies were done with a Beckman DU spectrophotometer, using a hydrogen discharge lamp as ultraviolet source. Figure 8 shows that potassium diazomalonate has an absorption band in the region 240–280 mμ, with a maximum at 255 mμ; the three metal ions absorb very little in this wave length region.

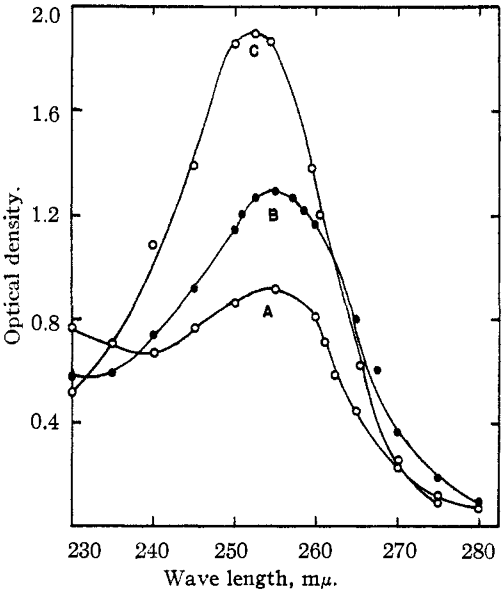

Fig. 8.—Ultraviolet absorption curves: A, 2 × 10^{-4} *M* $N_2C(COOK)_2$; B, same + 1 × 10^{-4} *M* $LaCl_3$; C, same + 1 × 10^{-4} *M* $AlCl_3$. A curve with 10^{-4} *M* $CeCl_3$ would almost coincide with B.

A mixture containing lanthanum chloride and diazomalonate in the molar ratio 1:2 decreases the absorption at 230 mμ, and intensifies it strongly in the 255 mμ band; cerium chloride gives an almost identical curve. Aluminum chloride intensifies the color much more, widens the band on the ultraviolet side, and shifts the maximum slightly. The behavior is characteristic of chelate and other complex formation[8]; there is often a considerable shift of the absorption band.

The method of continuous variation of Job is sometimes useful in finding the composition of a complex.[8] In the present case it was not found satisfactory with the lanthanum chelate. To obtain a maximum in the absorption-concentration curve, the optical density of the chelate would have to be much higher. One can, however, look for maximum deviation from the absorption-concentration curve of the diazomalonate alone.

Potassium diazomalonate was found to show excellent conformity with Beer's law at 255 mμ, up to 2 × 10^{-4} *M*, provided that measurements were made in slightly alkaline solution (5 × 10^{-4} *M* sodium hydroxide) to stabilize the salt. Conformity with Beer's law in pure water may be assumed, but experimental points were somewhat scattered because of slight decomposition, perhaps gas bubble formation. Even with lanthanum chloride present, duplication was somewhat erratic; the best results were obtained with cold solutions and rapid measurement.

When mixtures of diazomalonate and lanthanum chloride, having a constant total concentration of 2 × 10^{-4} *M*, are measured, there is pronounced deviation from Beer's law, as shown in Fig. 9. The point of maximum deviation cannot be fixed sufficiently accurately, however, to deduce the composition of the compound. Lanthanum hydroxide is too insoluble to repeat the experiment with even a trace of alkali present, to make the measurements more reproducible.

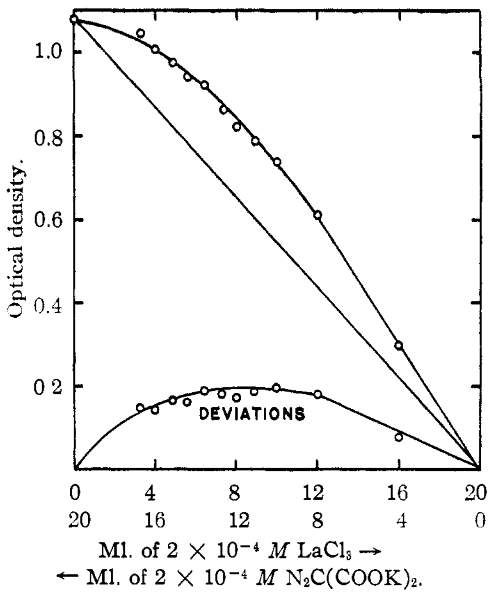

Fig. 9.—Deviations from Beer's law in mixtures of diazomalonate and lanthanum chloride, at 255 mμ.

It was hoped that by adding increasing amounts of metal salt to solutions containing a fixed amount of diazomalonate, a satisfactory "end-point" could be obtained. This was not the case; the optical density rises rapidly with small additions of salt, continues to rise more slowly with excess metal ion, with no sharp break in the curves.

Discussion

While the optical properties are inconclusive in establishing formulas of the chelates, they verify indirectly the evidence of the conductance titrations. The complexes are not weakly ionized salts, and, of course, are not merely electrostatic complexes. The conductance curves indicate some dissociation, and this is also shown by the fact that lanthanum hydroxide precipitates when traces of sodium hydroxide (about 10^{-5} *M*) are added, even with excess diazomalonate present.

No attempt was made to isolate the aluminum chelate, which is less dissociated, and apparently is considerably more soluble than the others. Because of its stability even in acid solution, it should be possible to study it more easily than the others.

It is difficult to picture a structural formula for these chelates. The resonant nature of aliphatic diazo groups implies that they are possible electron donors,[9] but no coördinate complexes or chelates have been reported in the literature so far as we are aware. Although the simple malonate ion does not chelate with these metal ions, and the diazo group is the determining factor, the carboxyl groups of the diazomalonate are no doubt involved.

Spatial considerations make it unlikely that the diazomalonate ion can act as a tridentate chelating agent with a single metal ion. Aside from the possible structure of the diazomalonate ion, the stripped aluminum ion is small (radius about 0.5 Å.) lanthanum and cerium ions are not large ($r \sim 1.1$ Å.).

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(8) Reference 7, p. 26.

(9) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 462.

It seems more probable that four of the six coördinating positions of the metal atom are occupied by carboxyl oxygens from diazomalonate ions, while the diazo groups cross-coördinate to other metal atoms. The simplest polymer thus formed would be a dimer, but the way would be open to higher polymerization. This might explain the gummy or tacky nature of the lanthanum precipitate described above, which is characteristic of some high polymers. It does not seem likely that the nature of the diazomalonate is essentially changed in the chelation process, as by formation of a bisdiazo compound.

There is no evidence as to why the aluminum chelate should be so much less subject to decomposition than the others. It is less dissociated into its parent ions, but dissociation is of minor importance with lanthanum and cerium ions, especially when these are present in excess. It is, of course, not unusual for chelates to be much more or much less reactive than the parent substances.[10]

We can conclude that chelate formation represses the general base catalysis, and in the presence of aluminum ion only the small amount of free diazomalonate in equilibrium with the complex can decompose. The lanthanum and cerium chelates, on the other hand, can react with acids, and the reaction may be subject to general acid catalysis.

[10] Reference 7, p. 64, and Chap. 8.

NEW YORK 3, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY]

Spectrophotometric Investigation of the Copper(II) Ion–Triethanolamine Complex

BY JOHN M. BOLLING[1] AND JAMES L. HALL

RECEIVED FEBRUARY 24, 1953

The deep blue complex ions existing in aqueous solutions of copper(II) ion and triethanolamine were studied, from *p*H 3 to *p*H 14 and at ionic strengths 0.03 and 0.120, by the methods of spectrophotometry and electrical migration. In dilute solutions copper(II) ion and triethanolamine form complex ions only in the ratio of 1:1. Variations in the light absorption with changes in *p*H are believed to be due to changes in the number of coördinated hydroxyl ions. At low values of *p*H migration experiments indicate a positively charged complex. As the *p*H is raised, a neutral complex is formed and at still higher values of *p*H, the complex becomes negatively charged. At *p*H 9.8 the colored complex does not migrate in the electric field and is assumed to be $Cu(OH)_2(H_2O)N(C_2H_4OH)_3$.

Introduction

Although a number of crystalline compounds have been prepared from aqueous solutions of triethanolamine and various copper(II) salts[2] there have been few attempts to determine the formulas of the complexes formed in aqueous solution. Yoe and Barton[3] studied the system copper(II) ion–triethanolamine in an attempt to develop a colorimetric analytical method for the determination of copper. They did not attempt to identify the entity that produced the deep blue color. Harvey, Tewksbury and Haendler[4] studied the system copper(II) ion–diethanolamine by the method of continuous variations as extended by Vosburgh and Cooper.[5] Their results were interpreted to indicate that ions are formed with copper to diethanolamine ratios of less than 1:3 and also with ratios greater than 1:3.

The present investigation was undertaken to obtain information regarding the composition of complexes formed between copper(II) ion and triethanolamine in aqueous solution.

Preliminary investigations showed that for solutions of copper(II) ion and triethanolamine the wave length of maximum optical density and the extinction coefficient at this wave length varied as the ratio of the two substances was changed. It was further found that at a fixed ratio of copper(II) ion to triethanolamine similar spectral variations occurred as acid or alkali was added. It was found that for corresponding copper(II) ion concentrations, the spectrum of a solution containing copper(II) ion and four equivalents of triethanolamine was almost identical with the spectrum of the compound $Cu(OH)_2{\cdot}N(C_2H_4OH)_3$ prepared by the method of Duff and Steer.[2b] For solutions made by adding only copper(II) salt and triethanolamine to water, at ratios of copper(II) ion to triethanolamine below 1:2, the complex or complexes formed were not stable enough to prevent precipitation of copper hydroxide or other hydrolysis products. At higher ratios of the amine to copper(II) ion or with added alkali the solutions were stable. The spectra of solutions containing varying ratios of copper(II) ion to triethanolamine at various fixed *p*H values and ionic strengths are reported here. Since these data indicate that the charge of the complex varies as *p*H is changed, the results of a series of migration experiments are also reported.

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[1] This paper is based upon a portion of the thesis by John M. Bolling in partial fulfillment of the requirements for the Ph.D. degree, June, 1952.

[2] (a) J. R. Anderson, "The Use of Alkanolamines in the Separation of Cobalt from Nickel and the Determination of Cobalt," M.S. Thesis, West Virginia University, Morgantown, W. Va., 1941, p. 35; (b) J. C. Duff and E. H. Steer, *J. Chem. Soc.*, 2861 (1932); (c) G. Garelli, *Atti. accad. sci. Torino, Classe Sci. Fis., Mat. Nat.*, **68**, 398 (1933); (d) F. Garelli, *Congr. intern. quim. pura y aplicada, 9th. Congr. Madrid*, **3**, 295 (1934); (e) F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, **63**, 570 (1933); (f) F. Garelli and A. Tettamanzi, *Atti. accad. sci. Torino, Classe Sci. Fis., Mat. Nat.*, **69**, 89 (1934); (g) F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, **64**, 474 (1934); (h) W. Hieber and E. Levy, *Z. anorg. allgem. Chem.*, **219**, 225 (1934); (i) A. Tettamanzi and B. Carli, *Gazz. chim. ital.*, **63**, 566 (1933); (j) A. Tettamanzi and B. Carli, *ibid.*, **64**, 315 (1934).

[3] J. H. Yoe and C. J. Barton, *Ind. Eng. Chem., Anal. Ed.*, **12**, 456 (1940).

[4] J. E. Harvey, C. I. Tewksbury and H. M. Haendler, THIS JOURNAL, **71**, 3641 (1949).

[5] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941).