enough in solution they undergo reactions resulting in decarboxylation. This observation also shows that carbon dioxide probably is not produced in the propagation step of the chain reaction. The low yield of carbon dioxide in the presence of iodine points to a relatively short life for this species. An alternative explanation of the source of carbon dioxide in uninhibited experiments would be that it arises from the reaction of solvent radicals with benzoate and that these solvent radicals are removed rapidly by iodine. However, such a reaction would represent a chain terminating step in the induced process and would make the induced reaction first order rather than three halves order with respect to peroxide.[3c]

Matheson[24] has suggested that radicals produced in the primary process may react with each other before leaving the solvent cage. This effect cannot be of great significance in chlorobenzene because the peroxide fragments are accounted for nearly quantitatively in products derived from reactions involving the solvent or iodine. It is still possible that a proximity effect does operate and that termolecular reactions involving two primary fragments and a foreign molecule do occur. This question is being further investigated in these laboratories.

Summary

The decomposition of benzoyl peroxide in benzene and chlorobenzene has been studied kinetically and by product analysis. The rate of peroxide decomposition is constant over a range of iodine concentrations but the relative rate of iodine uptake and the nature of the products depend on the iodine concentration. It is suggested that benzoyl hypoiodite is formed and reacts rapidly with the solvent in non-radical reactions which are catalyzed by iodine. The products of the reaction indicate the "cage effect" is unimportant in benzene solution. A maximum of ten per cent. of the theoretical amount of carbon dioxide is formed in the primary process.

RECEIVED OCTOBER 7, 1949

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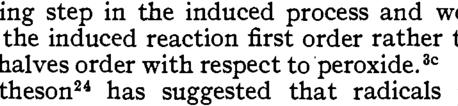
(24) Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY]

The Preparation and Properties of Some N,N'-Dialkylethylenediaminediacetic Acids

BY ALBERT E. FROST, JR.,[1] AND ARTHUR E. MARTELL

The purpose of this investigation was the preparation and study of the properties of a series of N,N'-dialkylethylenediaminediacetic acids, of the general formula



$$\mathrm{(R)(HOOC{-}CH_2)N{-}CH_2{-}CH_2{-}N(R)(CH_2{-}COOH)}$$

where R represents the *n*-butyl-, cyclohexyl-, *n*-octyl-, *n*-dodecyl- and benzyl-radicals. These symmetrically substituted ethylenediamine derivatives are of practical and theoretical interest since they constitute a new series of complexing agents and bear a structural similarity to the powerful chelating agent, ethylenediaminetetraacetic acid.

The N,N'-dialkylethylenediamines, utilized as intermediates in the synthesis of the N,N'-dialkylethylenediaminediacetic acids, were synthesized by the reaction of excess amine with ethylene dichloride by methods similar to that of Sebrell and Clifford.[2] The diamines were characterized as the dipicrates and the di-(phenylureides). These substances have been recently described.[3]

Condensation of sodium chloroacetate with the appropriate N,N'-dialkylethylenediamine was used for the preparation of N,N'-dibutyl-, N,N'-dioctyl-, N,N'-dibenzyl and N,N'-dicyclohexylethylenediaminediacetic acids, but gave poor yields. The dibutyl and dioctyl derivatives were also prepared by a variation of the method similar to that of Smith, *et al.*[4] Details of this preparation will be published later.[5] The condensation of ethylene dichloride with the respective N-alkylglycine was used as an additional method of preparation for the N,N'-dioctyl- and N,N'-didodecylethylenediaminediacetic acids. Although the yields reported are rather poor, it is felt that considerable improvement would result from a further study of these reactions. In Table I are summarized pertinent data on the products obtained.

The N,N'-dialkylethylenediaminediacetic acids are soluble in polar solvents and insoluble in non-polar solvents. The order of solubility in water is dibutyl- > dicyclohexyl- ≫ dibenzyl- > dioctyl- > didodecyl-. The latter three acids are only slightly soluble in water.

The tendency of the N,N'-dialkylethylenediaminediacetic acids to form complex salts with copper and calcium ions, taken as examples of the transition and alkaline earth metals, was

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[1] This paper is based on a dissertation presented by Albert E. Frost, Jr., to the Faculty of Clark University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1949.

(2) Sebrell and Clifford, U. S. Patent 1,948,317 (Feb. 20, 1934).

(3) Frost, Chaberek and Martell, THIS JOURNAL, **71**, 3842 (1949).

(4) Smith, Bullock, Bersworth and Martell, *J. Org. Chem.*, **14**, 355 (1949).

(5) Martell, Doran and Bersworth, unpublished.

TABLE I

N,N′-DIALKYLETHYLENEDIAMINEDIACETIC ACIDS

Alkyl	Formula	M. p.,[a] °C.	Mol. wt. Calcd.	Mol. wt. Found[b]	Nitrogen, % Calcd.	Nitrogen, % Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Butyl	$C_{14}H_{28}N_2O_4$	184–196	288	292	9.72	9.44	58.30	58.42	9.79	9.63
Cyclohexyl	$C_{18}H_{32}N_2O_4$	210–216	340	357	8.23	8.11	63.50	63.50	9.47	9.48
n-Octyl	$C_{22}H_{44}N_2O_4$	184–188	400	381	6.99	7.20	65.96	66.02	11.07	10.93
n-Dodecyl	$C_{30}H_{60}N_2O_4$	157–167	513	. . .	5.46	5.05	70.26	70.21	17.94	17.76
Benzyl	$C_{20}H_{24}N_2O_4$	230–235	356	332	7.86	8.06	67.39	67.37	6.79	6.69

[a] All compounds melted with decomposition. [b] Calculated from potentiometric data.

determined qualitatively by two methods. The first was a potentiometric method, similar to the quantitative procedure employed by Schwarzenbach and Ackermann[6] for the determination of the stability constants of ethylenediaminetetraacetic acid chelates. The second method involved a comparison of the ultraviolet absorption spectra of the disodium salts of the N,N′-dialkylethylenediaminediacetic acids in the presence of a stoichiometric amount of cupric chloride with the absorption spectra of the disodium salts and of cupric chloride alone.

The potentiometric method showed that all the N,N′-dialkylethylenediaminediacetic acids, with the exception of the dicyclohexyl derivative, formed strong chelates with cupric ions. This is indicated in Fig. 1, in which the inflection points of the acids in the presence of copper are displaced approximately twice the distance from the origin as the inflection point of the free acid. This is due to the acidification effect produced as a result of complex formation. The sharp initial rise in *p*H of the titration curves of the acids is attributable to the common-ion effect since the acids are only slightly dissociated. The appearance of only one inflection point in the titration curves of the N,N′-dialkylethylenediaminediacetic acids corresponds to the addition of one equivalent of base and therefore to the formation of the acid salt. The second inflection point, which corresponds to formation of the normal salt, does not appear, possibly because of extensive hydrolysis of the salt in the low concentrations employed in this investigation. The absence of the second inflection point indicates a very small value for the second ionization constants of these acids. It is likely that the acid salt is stabilized and hydrolysis of the normal salt is increased because of the formation of a hydrogen bridge having the structure

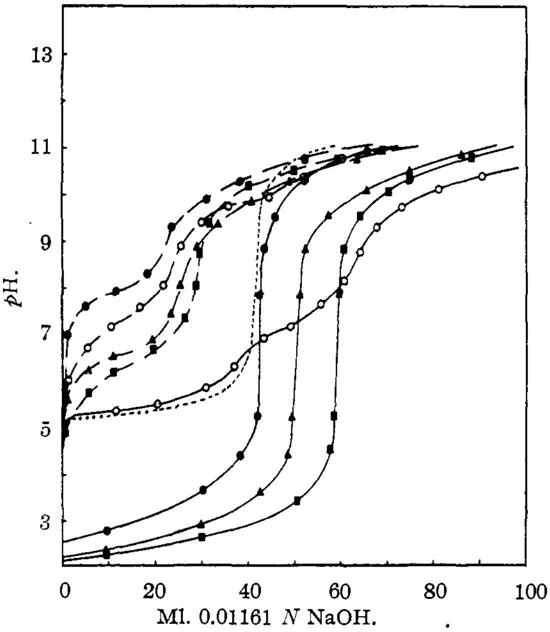
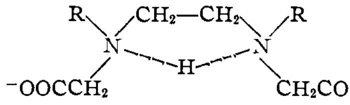


Fig. 1.—Titration curves: copper sulfate, - - - - - -; free acids, — — — —; acids with Cu⁺⁺, ————; N,N′-dibutylethylenediaminediacetic acid, ■; N,N′-dibenzylethylenediaminediacetic acid, ▲; N,N′-dioctylethylenediaminediacetic acid, ●; N,N′-dicyclohexylethylenediaminediacetic acid, O.



The existence of an inflection point corresponding to this acid salt, and of *pK* values (estimated from Fig. 1) of from 6.5 to 7.5 for the first ionization is more significant as evidence for interaction of the amino groups. This type of structure has been proposed by Schwarzenbach[6] to explain the unusual stability of the trialkali metal salts of ethylenediaminetetraacetic acid.

The N,N′-dicyclohexylethylenediaminediacetic acid represents an interesting case. No appreciable complex formation is indicated by the titration curve. The slight inflection point obtained in the presence of cupric ion does not indicate complex formation but is readily explained when this curve is compared with the titration curve of cupric sulfate alone. It is to be noted that the two curves run closely parallel up to a volume of about 40.50 ml. of base at which point the two curves intersect. Above this point, the curve for the N,N′-dicyclohexylethylenediaminediacetic acid with cupric ion corresponds closely to the curve of the free acid. The distance between the inflection points corresponds closely to the volume of sodium hydroxide necessary to attain the first inflection point (23.50 ml.) of the N,N′-dicyclohexylethylenediaminediacetic acid. Hence, it appears as though the first portion of this curve

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[6] Schwarzenbach and Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

represents the titration of the copper sulfate present and the second portion represents the titration of the acid. The lack of complex formation is probably due to the steric effect of the cyclohexyl groups. This interpretation was further strengthened upon examination of a molecular model of this substance.

The acidification effect of excess calcium salt on the *p*H titration curves was much weaker, indicating a much weaker tendency for complex formation. The titration curves for the N,N'-dioctyl- and N,N'-dicyclohexylethylenediaminediacetic acids alone and in the presence of calcium ions are given in Fig. 2. As expected, the dicyclohexyl derivative exhibited little or no complex formation. N,N'-Dioctylethylenediaminediacetic acid and N,N'-dibenzylethylenediaminediacetic acid (not shown) exhibited the strongest tendency toward complex formation with calcium ions. The calcium complex of the latter acid separated from solution as a white insoluble precipitate at a *p*H of 8.6.

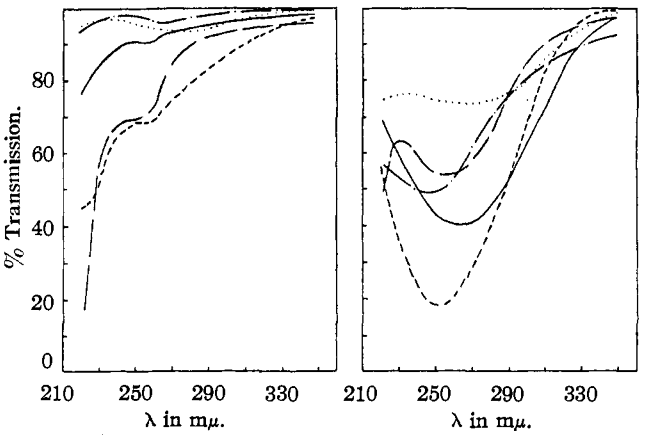

Fig. 3.—Absorption spectra of salts of N,N'-dialkylethylenediaminediacetic acids at 1.00×10^{-4} *M:* A, disodium salts; B, copper salts. Dibutyl, ———; dioctyl —·—·—; dibenzyl, — — —, didodecyl - - - - - - - - -, dicyclohexyl, ...

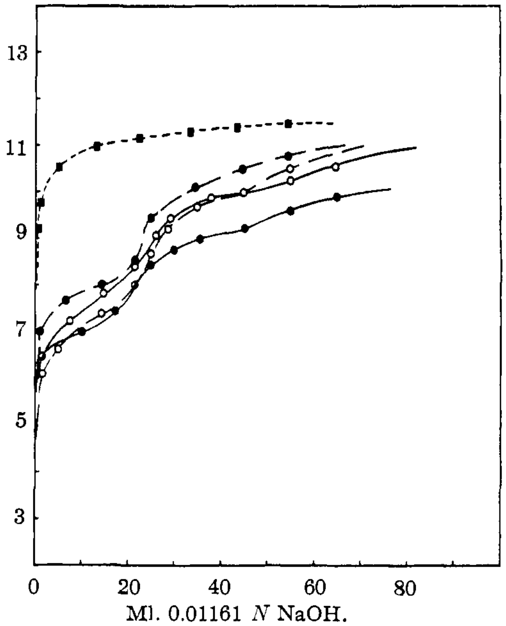

Fig. 2.—Titration curves: calcium chloride, - - - - - - - ; free acids, — — —; acids with Ca, ———; N,N'-dioctylethylenediaminediacetic acid, ●; N,N'-dicyclohexylethylenediaminediacetic acid, O.

Spectrophotometric data on the copper salts confirmed the results of the potentiometric method and gave more conclusive evidence that the N,N'-dicyclohexylethylenediaminediacetic acid undergoes only slight complex formation with copper. These results are plotted in Fig. 3. Aqueous and alcoholic solutions of cupric chloride exhibit only negligible absorption in the ultraviolet region from 220–350 mμ in the concentrations employed in this investigation. The disodium salts on the other hand showed some absorption in this region with the exception of the disodium salts of the dibenzyl and didodecyl derivatives, which showed considerable absorption. The absorption curves obtained by plotting the per cent. transmission as ordinate against the wave length in mμ as abscissa exhibit a broad band in the region 255–260 mμ with the exception of the disodium salt of N,N'-dicyclohexylethylenediaminediacetic acid which shows a much lower absorption at 280 mμ.

The transmission curves in the region 220–350 mμ for the disodium salts of the N,N'-dialkylethylenediaminediacetic acids in the presence of a stoichiometric amount of cupric chloride show much more intense absorption bands than those of the disodium salts alone. This may be interpreted as being due to the formation of a complex salt between the acids and the cupric ion. The wave length of maximum absorption for the complex and for the corresponding alkali metal salt is the same in every case except for that of the N,N'-dicyclohexylethylenediaminediacetic acid which is shifted toward shorter wave lengths, 260 mμ.

Experimental

N,N'-Dicyclohexylethylenediaminediacetic Acid.—An aqueous solution of 55.0 g. of sodium chloroacetate in 150 ml. of water was added dropwise with vigorous stirring over a period of two hours to a solution of 50.0 g. of N,N'-dicyclohexylethylenediamine in 100 ml. of alcohol at reflux temperature. The heating and stirring were continued for an additional two hours. The mixture was then evaporated to dryness under reduced pressure, the residue dissolved in a minimum amount of hot water, cooled, filtered and the filtrate evaporated to dryness *in vacuo*. The resulting viscous brown residue was extracted with absolute alcohol, filtered, and the filtrate evaporated to dryness under reduced pressure. This procedure was repeated, and the viscous residue was taken up in acetone. The desired product which separated out was filtered off and the filtrate distilled to dryness under reduced pressure. The addition of acetone, filtration and evaporation were repeated until crystallization no longer occurred. The total yield of slightly impure acid obtained in this fashion was 20.0 g. (26%). The acid was purified by four recrystallizations from absolute alcohol.

N,N′-Dibutylethylenediaminediacetic Acid.—The procedure employed was the same as that given for the N,N′-dicyclohexylethylenediaminediacetic acid: 25.0 g. of N,N′ dibutylethylenediamine in 150 ml. of water reacted with 35.0 g. of sodium chloroacetate to give 6.0 g. (15%) of N,N′-dibutylethylenediaminediacetic acid. Five recrystallizations from absolute alcohol gave fine colorless crystals of pure material.

N,N′-Dibenzylethylenediaminediacetic Acid.—By the same procedure, 24.03 g. (0.1 mole) of N,N′-dibenzylethylenediamine in 100 ml. of alcohol reacted with 23.3 g. (0.2 mole) of sodium chloroacetate to give 4.25 g. (12%) of N,N′-dibenzylethylenediaminediacetic acid.

N,N′-Didodecylethylenediaminediacetic Acid.—To 26.54 g. of the sodium salt of N-dodecylglycine in 200 ml. of water, 4.94 g. (0.05 mole) of ethylene dichloride was added dropwise over a period of one hour. The mixture was then refluxed for one and one-half hours after which 4.94 g. more of ethylene dichloride was added and the mixture refluxed for thirty-two more hours. To minimize foaming of the mixture, a current of air was passed over the surface throughout the entire reaction. Evaporation of the mixture to dryness *in vacuo* produced a slightly yellow residue which was ground to a fine powder and extracted with absolute alcohol. The solution was evaporated to dryness under reduced pressure. This resulted in the isolation of a viscous residue which was obtained in crystalline form by the addition of acetone; 10.30 g. (20%) of impure material was thus obtained. The impure N,N′-didodecylethylenediaminediacetic acid was purified by two recrystallizations from a 70% acetone–30% water solution.

Potentiometric Method.—One hundred milligrams of the N,N′-dialkylethylenediaminediacetic acid was dissolved in 100 ml. of water and titrated with standard sodium hydroxide (approximately 0.0100 *N*). The *p*H was determined with the aid of a Beckmann model G *p*H meter. To test for complex formation with copper, stoichiometric amounts of cupric sulfate were added to the solution of the N,N′-dialkylethylenediaminediacetic acid and the resulting solution titrated as outlined. Complex formation with calcium was determined in the same fashion; the ratio of calcium chloride to N,N′-dialkylethylenediaminediacetic acid used was 15 to 1. In cases where the acid was only slightly soluble in water, the titrations were carried out on a vigorously stirred suspension of the acid.

Spectrophotometric Method.—The absorption spectra were determined by means of a Beckmann model DU photoelectric quartz spectrophotometer. All measurements were made in the ultraviolet region (220–350 mμ) with quartz cells having a light path of 1 cm.

TABLE II

ABSORPTION DATA

COPPER CHELATES OF N,N′-DIALKYLETHYLENEDIAMINEDIACETIC ACIDS

Alkyl	Obs. max. in mμ	$E \times 10^3$	Solvent
Butyl	260	3.78	Water
Cyclohexyl	260	1.50	Water
Octyl	245	3.40	Ethanol
Dodecyl	250	7.14	Ethanol
Benzyl	255	2.70[a]	Water

[a] The extinction varied somewhat with concentration in this case. Otherwise Beer's law seemed to hold.

Acknowledgment.—The authors express their appreciation to F. C. Bersworth of Framingham, Massachusetts, for financial support for this research. The choice of the topic was made with his full coöperation, and the work was greatly aided by his continued interest and advice.

Summary

The preparation of N,N′-dialkylethylenediaminediacetic acids from dibutyl-, dioctyl-, didodecyl-, dicyclohexyl- and dibenzylethylenediamine is described. Titration and absorption spectra studies indicated that all the amino acids with the exception of the dicyclohexyl derivative formed strong chelates with copper ions, while titration data indicated only weak chelate-formation with calcium ions.

BERKELEY, CALIF. RECEIVED NOVEMBER 25, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Mechanical Properties of Substances of High Molecular Weight. VI. Dispersion in Concentrated Polymer Solutions and its Dependence on Temperature and Concentration

BY JOHN D. FERRY

In previous studies of the rigidities of concentrated polystyrene[1] and polyisobutylene[2] solutions, derived from measurements of transverse wave propagation, the dependence on frequency appeared to be small over a limited frequency range; it was ignored except in the more dilute polystyrene solutions, where an effort was made to extrapolate to a limiting high frequency value based on the assumption of a Maxwell model. On this basis, it was found that the rigidity was an exponential function of the reciprocal absolute temperature and was proportional to the third power of the volume concentration.

Subsequent measurements on solutions of polyvinyl acetate in various solvents,[3] of polystyrene in decalin,[4] and of a styrene–maleic anhydride copolymer in dioxane–water mixtures[5] have shown a dispersion which cannot be ignored; the wave rigidity,[2] $\tilde{G}$, increases monotonically with frequency. Also, solutions of polystyrene in xylene have been re-examined in larger cells than used previously[1]

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(1) J. D. Ferry, THIS JOURNAL, **64**, 1323, 1330 (1942).

(2) J. N. Ashworth and J. D. Ferry, *ibid.*, **71**, 622 (1949).

(3) W. M. Sawyer and J. D. Ferry, unpublished.

(4) L. D. Grandine, Jr., and J. D. Ferry, unpublished work.

(5) D. C. Udy and J. D. Ferry, unpublished work.