cult to maintain an adequate current through the solution. After electrolyzing for several hours with the current ranging from 50 to 1 ma. 7.9 cc. of gas was collected having a molecular weight of 22.14, which corresponds to 77.46% of nitrogen, assuming the remaining gas to be hydrogen. It does not seem possible to ascribe the results with sodium germanyl with platinum electrodes to the electrolysis of sodium amide. It seems more likely that substances are formed by interaction of the germanyl ion with sodium amide that lead to the observed results.

Summary

1. Methyl-, ethyl- and propylgermanes have been prepared by the reaction of sodium germanyl with the appropriate alkyl halides in liquid ammonia solution.

2. The reaction of methylene bromide with sodium germanyl is complex; the chief product is methylgermane.

3. Potassium germanyl has been prepared by reaction of monogermane with the metal in liquid ammonia solution. One mole of potassium germanyl is soluble in 4.604 moles of ammonia; the vapor pressure of the saturated solution is 20.4 cm. at −33.3°.

4. On electrolyzing sodium germanyl between a platinum anode and a mercury cathode, a reaction occurs at the anode: $6GeH_3^- + 2NH_3 = 6GeH_4 + N_2 + 6e^-$. When electrolysis of the salt is substantially complete, hydrogen and nitrogen are evolved in a molar ratio of 3/1; ammonia is electrolyzed.

On electrolysis of sodium germanyl between two platinum electrodes, hydrogen and nitrogen are evolved in a molar ratio of 3/1. A small amount of germane is evolved initially.

5. On electrolyzing sodium amide between a platinum anode and mercury cathode, little current passes because of the low solubility of the amide. A small quantity of gas was evolved of molecular weight 22, probably nitrogen admixed with hydrogen.

PROVIDENCE, R. I. RECEIVED AUGUST 25, 1949

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

The Kinetics of the Decomposition of Malonamic Acid in Aqueous Solutions

BY GEORGE A. HALL, JR.[1]

In a recent paper on the decomposition of malonic acid in aqueous solutions[2] it was suggested that the mechanism of the reaction involved the simultaneous first order decomposition of the unionized acid and of the acid malonate ion. It was of interest then to carry out a similar kinetic study on the decomposition of malonamic acid, the half amide of malonic acid. The results obtained might lend further support to the mechanism proposed for the malonic acid and would be of interest in observing the effect of substitution on the reaction rate.

This paper reports a study of the effect of changing *p*H on the rate of decomposition of malonamic acid. The results obtained are in agreement with the mechanism proposed for malonic acid.

Experimental

Materials.—Malonamic acid was prepared from diethyl malonate by the method of Galat.[3] The product obtained had a neutral equivalent of 101.9 (calcd. 103.1). The water used as a solvent was doubly distilled and of conductivity grade. The *p*H of the solution was varied by using either standard hydrochloric acid or sodium hydroxide solutions as solvents.

Procedure.—The rate of reaction was followed by the previously described procedure[1] of titrating the undecomposed acid. For those solutions containing hydrochloric acid or sodium hydroxide suitable corrections had to be made for the amounts of these substances present. The fact that the acidity of the solution decreased in the expected manner during the course of an experiment was taken as evidence that the reaction was indeed the decarboxylation of the acid since the only alternative reaction would have formed acetic acid and formamide with no change in acidity with time. Qualitative tests on the reacting solutions failed to detect the presence of ammonia which would have been formed had the amide hydrolyzed. The *p*H measurements were made at 25° on samples of the solutions used for the rate experiments with a Beckman glass electrode *p*H meter.

Results

The rate of decomposition of malonamic acid was measured at temperatures of 80 and 90° at concentrations of 0.01 and 0.1 *M* together with sufficient hydrochloric acid or sodium hydroxide

TABLE I

THE EFFECT OF CHANGING *p*H ON THE DECOMPOSITION OF MALONAMIC ACID

Initial concn., m./l.	Concn. of added substance, m./l.	*p*H	k_{80} sec.$^{-1}$ × 10^6	k_{90} sec.$^{-1}$ × 10^6	E_{80-90}, kcal.
0.0901	0.2045[a]	0.80	1.78	6.81	34.2
.0923	.1141[a]	0.91	1.78	6.79	34.1
.00902	.0474[a]	1.34	1.79	6.78	33.9
.00846	.0255[a]	1.51	1.79	6.69	33.5
.00885	.00630[a]	2.33	1.53	5.89	34.3
.00898	......	2.88	1.27	5.26	36.2
.00864	.00068[b]	2.98	1.22	4.74	34.5
.00845	.00106[b]	3.11	1.13	4.62	35.8
.00893	.00288[b]	3.41	0.967	3.90	35.5
.00808	.00346[b]	3.59	.838	3.32	35.0
.00834	.00479[b]	3.86	.568	2.11	33.4
.00850	.00528[b]	3.94	.468	1.92	35.9
.00807	.00598[b]	4.12	.343	1.27	33.3
.00847	.00699[b]	4.33	.216	.845	34.7

[a] HCl added. [b] NaOH added.

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[1] West Virginia University, Morgantown, W. Va.

[2] Hall, THIS JOURNAL, **71**, 2691 (1949).

[3] Galat, *ibid.*, **70**, 2596 (1948).

to give an over-all *p*H range of 0.8 to 4.33. At higher *p*H values the rate became too low to measure. The data are given in Table I.

It was found that while each experiment gave a good first order rate constant, the values of the rate constant increase with decreasing *p*H and eventually level off at a constant value. The variation of the rate constant with *p*H is shown in Fig. 1. The behavior of malonamic acid is thus seen to be very similar to that of malonic acid except that malonic acid shows another region of constancy in the value of the rate constant at higher *p*H values.[2] The apparent activation energies are essentially constant with change in *p*H.

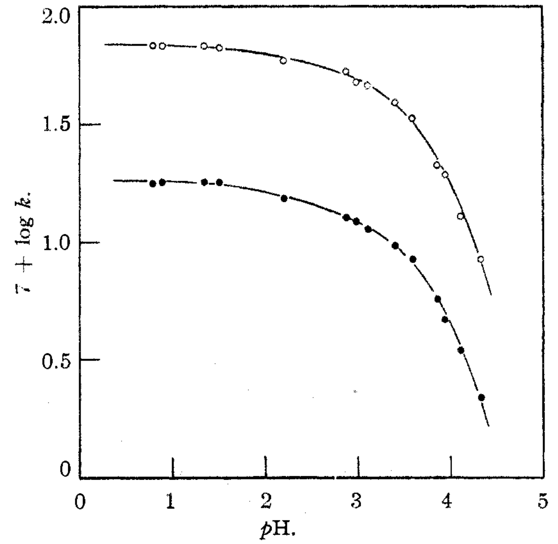

Fig. 1.—The variation of the rate constant for the decomposition of malonamic acid with *p*H: ○, 90°; ●, 80°.

Discussion

Since the behavior of malonamic acid is apparently very similar to that of malonic acid it seems likely that the mechanism for malonamic acid cannot be too different from the one proposed for malonic acid involving the simultaneous decomposition of the un-ionized acid and the acid malonate ion.[2] However malonamic acid in a solution of a *p*H of 6, where only 0.4% of the acid is not ionized, showed no appreciable decomposition at the end of 1800 minutes at 90°. This corresponds to an upper limit for the rate constant for the malonamate ion of 10^{-8} sec.$^{-1}$ which is zero within the error in the determinations of the experimental constants. Hence the only significant reaction occurring in the malonamic acid solutions is

$$H_2NCOCH_2COOH \longrightarrow CO_2 + H_2NCOCH_3$$

The observed rate constant should then be expressed by the relation

$$k = k_1(1 - x/a)$$

where k_1 is the rate constant for the decomposition of the un-ionized acid, a is the stoichiometric acid concentration, and x is the concentration of the malonamate ion. This relation was obtained by setting k_2, the rate constant for the malonamate ion, equal to zero in the equation derived for the decomposition of malonic acid.[2] Figure 2 shows a plot of k against the quantity x/a (calculated using the value of 2.28×10^{-4} for the dissociation constant of the acid at 25°[4]) for which the above relation predicts a linear plot. It is seen that the agreement is fairly good and that apparently the mechanism proposed is reasonable. The values of k_1 obtained from the intercepts at $x/a = 0$ of the line in Fig. 2 and its counterpart at 80° are 1.8×10^{-6} sec.$^{-1}$ at 80° and 6.8×10^{-6} sec.$^{-1}$ at 90° with an apparent activation energy of 33.8 kcal. It is to be noted that the rate constants are significantly lower than those reported for malonic acid.[2]

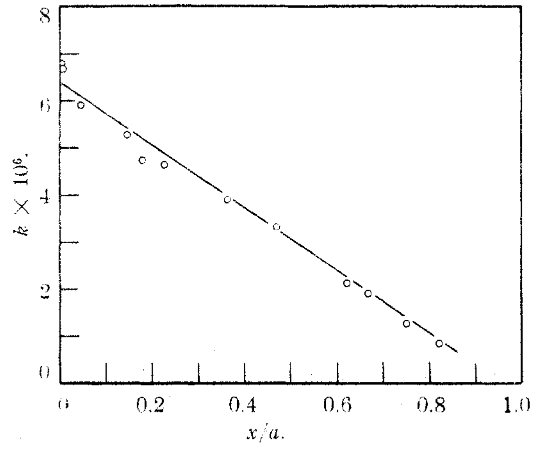

Fig. 2.—Rate constants for the decomposition of malonamic acid at 90° *vs.* the quantity x/a

The results of this study can be used to gain some insight into the mechanism of the decomposition of the acid malonate ion. While un-ionized malonic acid undergoes decomposition, the malonate ion shows no decomposition over long periods of time at relatively high temperatures.[5] It is thus reasonable to assume that the acid malonate ion decomposes by losing carbon dioxide from that carboxyl group which is not ionized. The data obtained in the malonic acid studies, however, provide no indication of which carboxyl group is decomposing. Since the malonamate ion which has no un-ionized carboxyl group is found not to decompose it is possible to conclude that it is indeed the un-ionized carboxyl group which loses carbon dioxide in the decomposition of the acid malonate ion.

Summary

1. The rate constant for the decomposition of malonamic acid was found to increase up to a maximum value with decreasing *p*H.
2. The observed change in rate constant was

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(4) Jeffery and Vogel, *J. Chem. Soc.*, 1101 (1934).

(5) Fairclough, *J. Chem. Soc.*, 1186 (1938).

found to be consistent with a mechanism in which only the un-ionized malonamic acid undergoes decomposition.

MADISON, WISCONSIN RECEIVED APRIL 10, 1950

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Decomposition of Benzoyl Peroxide in the Presence of Iodine. II. In Carbon Tetrachloride Solution[1,2]

BY GEORGE S. HAMMOND AND LOUIS M. SOFFER

The first paper in this series reported the results of a study, by product analysis and kinetics, of the decomposition of benzoyl peroxide in the presence of iodine in the aromatic solvents benzene and chlorobenzene.[3] The results were found to be understandable and compatible with earlier work with peroxides if it was assumed that benzoate radicals produced in the primary process react with iodine to give the unstable compound, benzoyl hypoiodite, which was rapidly destroyed in non-radical reactions with the aromatic solvents. The object of the present investigation was to extend the study to decomposition in carbon tetrachloride solution containing iodine. It was hoped to obtain further information concerning both the primary process and the chemistry of the reaction between iodine and the benzoate radical by working in a solvent which not only shows very different reactivity toward certain free radicals,[4] but would also be expected to be unreactive toward electrophilic attack by the postulated intermediate.

Boëseken and Gelissen[5] reported among the products of the decomposition of benzoyl peroxide in carbon tetrachloride, ω-trichloro-*p*-toluic acid, carbon dioxide, chlorobenzene, hexachloroethane and phosgene. Kharasch and Dannley[6] in their study of the thermal decomposition of di-α-naphthoyl peroxide in carbon tetrachloride isolated carbon dioxide, hexachloroethane and α-chloronaphthalene as primary reaction products. α-Naphthoic acid, naphthalene-1,4-dicarboxylic acid and 4′-carboxy-1′-naphthyl 1-naphthoate were found as products resulting from hydrolysis of the reaction mixture.

Perret and Perrot,[7] studying the decomposition in the same solvent in the presence of iodine and olefins, observed that relatively little carbon dioxide was evolved and obtained high yields of the corresponding diol dibenzoates. The isolation of 2-iodocyclohexyl benzoate from cyclohexene and the fact that this material reacted further to yield the corresponding dibenzoate suggested to these investigators that benzoyl hypoiodite was involved.

Experimental

Benzoyl peroxide was twice recrystallized by dissolving in chloroform and pouring the solution into methanol; assay, 99.5% minimum.[8]

Iodine, Baker and Adamson reagent grade, was used without further purification.

Carbon Tetrachloride, Baker and Adamson reagent grade, was dried over anhydrous sodium sulfate and redistilled.

Product Analysis. (A).—A solution of 10.0 g. of iodine (0.0394 mole), 10.0 g. of benzoyl peroxide (0.0413 mole) in 160 ml. of carbon tetrachloride was placed in a 250-ml. glass bomb, the contents swept with dry nitrogen, sealed, and immersed in a thermostat at 79.0 ± 0.05° for 36–48 hours or until virtually all the peroxide had decomposed. After opening, a small amount (5–10 mg.) of a fine, light-colored sediment was removed by decantation through glass wool. A 10-ml. sample was withdrawn. The remaining solution (141 ml.) was decolorized with a few ml. of concentrated aqueous sodium thiosulfate, and then fractionated to remove most of the carbon tetrachloride–water azeotrope (66°). The residue was extracted with small portions of 100 ml. of aqueous sodium bicarbonate. After concentration, acidification and recrystallization 0.27 g. of benzoic acid (m. p. 119°) was obtained (no depression with authentic sample). Ether extraction of aqueous mother liquors yielded a further 0.15 g., melting at 119°.

The insoluble fraction from the aqueous bicarbonate extraction was fractionated under close observation, assuring the constant presence of water until all the carbon tetrachloride had distilled, as shown by the sudden rise in temperature above 67°. The two layers in the flask were separated. The lower yellow, oily layer, A, was steam distilled until the distillate was clear (500 ml. of distillate collected). On standing overnight the mixture separated into two layers, water and iodobenzene. After separation and drying, 7.1 ml. of iodobenzene was obtained (micro b. p. 188°, n^{20}_{D} 1.618, m. p. of *p*-nitro derivative 171°). Layer B was found to contain a negligible amount of iodobenzene. The yellowish semi-solid residue from the steam distillation of A could not be crystallized. Saponification in the usual way followed by recrystallization yielded 0.15 g. of benzoic acid. The phenolic component was isolated as 2,4,6-tribromophenol (m. p. 92.5–93.5°, no depression with authentic sample). Acetylation of the latter yielded 2,4,6-tribromophenyl acetate (m. p. 82°). This substance showed a definite depression when mixed with 2,5-dibromo-4-iodophenyl acetate (m. p. 87°).

(B).—A solution of 5.0 g. of iodine (0.019 mole), 5.0 g. of benzoyl peroxide (0.021 mole), 2 ml. of water and 80 ml. of carbon tetrachloride was prepared and treated exactly as in run (A). The bomb was removed from the thermostat after 41 hours. There was no solid present. The remaining solution (81.5 ml.) was decolorized with aqueous thiosulfate. After fractionation, a mass of white

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(1) Presented before the Physical and Inorganic Division at the 117th Meeting of the American Chemical Society, Detroit, April, 1950.

(2) We gratefully acknowledge the financial support of this work by the Office of Naval Research.

(3) Hammond, THIS JOURNAL, **72**, 3737 (1950).

(4) Mayo, *ibid.*, **65**, 2324 (1943).

(5) Boëseken and Gelissen, *Rec. trav. chim.*, **43**, 869 (1924).

(6) Kharasch and Dannley, *J. Org. Chem.*, **10**, 406 (1945).

(7) Perret and Perrot, *Helv. Chim. Acta*, **28**, 558 (1945).

(8) Liebhafsky and Sharkey, THIS JOURNAL, **62**, 190 (1940).