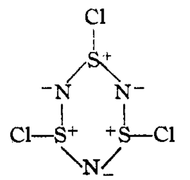
their respective formulas. Thus when sulfur nitride is hydrogenated the resulting substance $H_4N_4S_4$,[4] presumably has a ring structure with alternate sulfur and (imino) nitrogen atoms. (The structure of $H_4N_4S_4$ reported by Jaeger and Zanstra[5] cannot be correct for the same reasons which we have discussed in regard to their structure of sulfur nitride.) In the formation of the thiotrithiazyl ion[9] $(N_3S_4)^+$ on boiling sulfur nitride with acetyl chloride, the "cradle" structure with its eight-ring is apparently torn open, giving rise to an ion having possibly the following chain structure: $S{=}N-{}^{+}S{=}N-S-N{=}S$, which derives its stability from resonance between two identical bond structures. The molecule is also degraded on chlorination with the formation of $(SNCl)_3$,[4] which possibly has the structure



The existence of $(SNCl)_4$ is probable, although it has not been definitely established. Regarding the formation of coördination compounds of sulfur nitride with metallic chlorides such as $SnCl_4$ and $MoCl_4$,[32] Arnold, Hugill and Hutson's explanation[8] in terms of a "unique" sulfur atom in the sulfur nitride molecule is by no means necessary.

We wish to thank Dr. V. Schomaker for helpful suggestions and illuminating discussions.

Summary

Sulfur (S_8), orpiment (As_4S_6), sulfur nitride (S_4N_4), and realgar (As_4S_4) were studied by the method of electron diffraction. The S_8 molecule is a regular puckered-ring with $S-S = 2.07 \pm 0.02$ Å. and $\angle S-S-S = 105 \pm 2°$, and it exhibits a rather large amplitude of thermal vibration. Orpiment sublimes at high temperatures, presumably to give As_4S_6 molecules which have the As_4O_6 structure and the following dimensions: $As-S = 2.25 \pm 0.02$ Å., $\angle As-S-As = 100 \pm 2°$ ($\angle S-As-S = 114 \pm 2°$). The molecular structures of sulfur nitride S_4N_4 and realgar As_4S_4 cannot be established with certainty from the electron diffraction data alone, although several structures proposed by previous workers are definitely eliminated. We have shown that cradle-shaped configurations of an alternating eight-ring lead to satisfactory models. For sulfur nitride this "cradle" model consists of a bisphenoid of sulfur atoms and a square of nitrogen atoms, with $N-S = 1.62 \pm 0.02$ Å., $S-S = 2.69$ Å., $\angle S-N-S = 112°$ and $\angle N-S-N = 106°$. For realgar the model consists of a bisphenoid of arsenic atoms and a square of sulfur atoms with $As-S = 2.23 \pm 0.02$ Å., $As-As = 2.49 \pm 0.04$ Å., and $\angle As-S-As = 101 \pm 4°$ ($\angle S-As-S = 93°$; $\angle S-As-As = 100°$). These results are discussed, special attention being given to the unconventional sulfur nitride structure and its relation to the realgar structure.

PASADENA 4, CALIFORNIA RECEIVED JANUARY 24, 1944

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

The Behavior of γ-Keto- and Aldehydo-Acid Derivatives at the Dropping Mercury Electrode. I. Esters and Anhydrides of 2-Benzoylbenzoic Acid

BY S. WAWZONEK,[1] H. A. LAITINEN AND S. J. KWIATKOWSKI

γ-Keto- and aldehydo-acids are of special interest since they and their derivatives can exist in two isomeric forms. Assignment of structure to these forms has been concerned mainly with the isomeric methyl and ethyl esters and has been accomplished both by chemical and physical means. Physical methods such as absorption spectra[2] and the use of refractive indices[3] have in general required both isomeric forms. Chemical methods used have been mainly generalizations. The most important of these is the rapid hydrolysis of the cyclic ester by means of concentrated sulfuric acid to give highly colored solutions in contrast to slow hydrolysis and a weaker color in the case of the normal esters.[4] Recent investigations have shown this test to be unsatisfactory in numerous cases.[5]

In this paper the use of the polarograph as a means of assigning structures to the esters of 2-benzoylbenzoic acid will be presented. The behavior of certain anhydrides at the dropping mercury electrode will likewise be mentioned. The study of certain amides of 2-benzoylbenzoic acid is described in the accompanying paper.[6] Work with other types of γ-keto- and aldehydo-acid derivatives is now in progress.

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[1] Present address: Department of Chemistry, University of Tennessee, Knoxville, Tennessee.

[2] Hantzsch and Schwiete, *Ber.*, **49**, 215 (1916).

[3] (a) Egerer and Meyer, *Monatsh.*, **34**, 69 (1913); (b) von Auwer and Heinze, *Ber.*, **52**, 584 (1919).

[4] Meyer, *Monatsh.*, **25**, 477 (1904).

[5] (a) Blicke and Swisher, THIS JOURNAL, **56**, 904 (1934); (b) Newman and McCleary, *ibid.*, **63**, 1537 (1941).

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Results

The behavior of various esters and anhydrides of 2-benzoylbenzoic acid, their reduction products and related compounds was studied in both unbuffered and buffered media. A summary of the observed half-wave potentials and individual diffusion current constants in the various solutions is given in Tables I and II.

TABLE I

HALF-WAVE POTENTIALS AND INDIVIDUAL DIFFUSION CURRENT CONSTANTS OF 2-BENZOYLBENZOIC ACID DERIVATIVES AND RELATED COMPOUNDS IN VARIOUS SOLUTIONS

Compound	$\pi_{1/2}$ vs. S. C. E., volts	i_d, microamperes	C, millimoles/liter	i_d/C, microamperes/millimole/liter
0.1 M Tetrabutylammonium Iodide, 50% Dioxane				
Esters				
n-Methyl	1.51	3.51	0.87	4.03
	1.94	3.44		3.95
ψ-Methyl	1.85	5.33	0.83	6.53
n-Ethyl	1.49	4.95	1.34	3.86
	1.92	4.49		3.51
ψ-Ethyl	1.85	8.58	1.65	5.22
Phenyl (m. p. 83°)	1.30	3.69	1.07	3.45
	1.92	4.09		3.82
Phenyl (m. p. 162–163°)	1.53	2.85	0.77	3.70
	1.91	2.75		3.57
Thiophenyl (m. p. 112–113°)	1.17	3.75	1.15	3.36
	1.67	1.47		1.32
	1.92	2.92		2.62
Thiophenyl (m. p. 119–121°)	1.41	4.46	1.36	3.27
	1.91	4.16		3.05
β-Naphthyl (m. p. 103–105°)	1.25	3.02	1.00	3.02
	1.94	3.82		3.82
β-Naphthyl (m. p. 198–199°)	1.27	3.95	1.08	3.66
4-Bromophenyl (m. p. 92–94°)	1.22 max.	4.15	1.05	3.95
4-Bromophenyl (m. p. 170–172°)	1.47	4.29	1.05	4.09
	1.93	4.39		4.18
3-Phenylphthalide	1.89	3.90	1.00	3.90
Benzophenone	1.48	5.50	1.38	3.98
4′-Hydroxydiphenylphthalide	1.88	5.49	1.74	3.16
Ethyl benzoate	2.18	7.70	1.01	7.62
2-Benzoylbenzoic acid	1.11	1.87	1.00	1.87
	1.60	1.87		1.87
Benzoic acid	1.87	2.34	1.10	2.12
Acetic 2-benzoylbenzoic anhydride	1.48	3.90	1.00	3.90
	1.92	2.99		2.99
2-Benzoylbenzoic anhydride	1.28	2.73	1.00	2.73
	1.58	3.05		3.05
	1.90	2.60		2.60
3,3′-Diphenyldiphthalyl sulfide	1.35	2.92	0.82	3.56
	1.56	1.20		1.46
	1.91	1.90		2.32
0.1 M Hydrochloric Acid, 50% Dioxane				
2-Benzoylbenzoic acid	0.95	5.89	1.15	5.12

TABLE II

HALF-WAVE POTENTIALS AND INDIVIDUAL DIFFUSION CURRENT CONSTANTS OF 2-BENZOYLBENZOIC ACID DERIVATIVES IN BUFFERED MEDIA: BUFFER I

Compound	$\pi_{1/2}$ vs. S. C. E. volts	i_d, micro amperes	C, millimoles/liter	i_d/C, micro amperes/millimole/liter
Anthraquinone	0.63	2.61	1.06	2.50
Esters				
n-Methyl	1.33	4.71	1.19	3.96
ψ-Methyl	1.82	6.22	1.10	5.16
n-Ethyl	1.39	8.04	1.99	4.02
ψ-Ethyl	1.87	5.43	1.24	4.37
Phenyl (83°)	1.27	4.61	1.23	3.75
Phenyl (162–163°)	1.59	4.50	1.31	3.45
Thiophenyl (112–113°)	1.22	6.16	1.66	3.73
	1.47	2.38		1.43
	1.63	3.37		2.90
Thiophenyl (119–121°)	1.43	2.89	1.17	2.48
β-Naphthyl (103–105°)	1.30	3.49	1.07	3.26
β-Naphthyl (198–199°)	1.29	2.34	1.05	2.23
4-Bromophenyl (92–94°) ·	1.29	4.59	1.14	4.03
4-Bromophenyl (170–172°)	1.55	4.84	1.28	3.78
Benzophenone	1.33	6.28	1.38	4.55
Acetic 2-benzoylbenzoic anhydride	1.44	6.43	1.89	3.38
2-Benzoylbenzoic anhydride	1.20	5.57	0.82	6.75
3,3′-Diphenyldiphthalyl sulfide	1.15	3.71	0.82	4.53
2-Benzoylbenzoic acid	1.44	3.61	0.89	4.06
BUFFER II				
Anthraquinone	0.76	2.65	1.06	2.50
Esters				
n-Methyl	1.51	4.19	1.13	3.75
ψ-Methyl	1.84	7.08	1.43	4.95
n-Ethyl	1.48	7.77	2.12	3.67
ψ-Ethyl	1.85	12.12	2.38	5.10
Phenyl (83°)	1.28	3.08	1.10	2.80
	1.53	0.79		0.72
	1.91	3.42		3.11
Phenyl (162–163°)	1.59	4.66	1.30	3.58
	1.93	1.28		0.99
Thiophenyl (112–113°)	1.15	4.12	1.29	3.20
	1.46	0.91		0.71
	1.69	1.32		1.02
Thiophenyl (119–121°)	1.42	4.02	1.36	2.96
	1.94	3.95		2.91
β-Naphthyl (103–105°)	1.29	4.99	1.65	3.03
	1.98	5.67		3.44
β-Naphthyl (198–199°)	1.30	4.19	1.18	3.55
	2.10	3.18		2.70
4-Bromophenyl (92–94°)	1.26	5.85	1.55	3.77

TABLE II (*Concluded*)

Compound	$\pi_{1/2}$ *vs.* S. C. E. volts	i_d, micro amperes	*C*, millimoles/liter	i_d/C, micro amperes/millimole/liter
4-Bromophenyl (170–172°)	1.55	3.35	0.95	3.54
Benzophenone	1.45	9.91	2.40	4.13
Acetic 2-benzoylbenzoic anhydride	1.52	5.17	1.50	3.42
	1.91	1.72		1.14
2-Benzoylbenzoic anhydride	1.27	1.61	0.72	2.25
	1.55	3.06		4.28
	1.89	1.06		1.48
3,3′-Diphenyl diphthalyl sulfide	1.28	2.88	0.69	4.16
	1.48	1.03		1.48
	1.91	1.57		2.26
2-Benzoylbenzoic acid	1.53	5.23	1.31	4.00

In general all of the compounds gave well-defined reduction waves. Maxima could be suppressed in most cases by means of gelatin. Addition of gelatin was noticed to cause a catalytic hydrogen discharge wave which decreased the voltage range of the buffers and prevented evaluation of waves at more negative potentials.

Absolute *p*H values for the buffers are not given because erratic behavior of hydrogen electrodes made accurate measurements impossible. Comparative values however were determined from the half-wave potentials obtained for anthraquinone. Buffer II was found to be 2.2 *p*H units more alkaline than buffer I.

Discussion of Results

An examination of the half-wave potentials obtained in 0.1 *M* tetrabutylammonium iodide–50% dioxane solution, in which a wide range of potential is possible, indicates that in general all the esters of 2-benzoylbenzoic acid are reduced to the same product, 3-phenylphthalide. A final wave of approximately 1.9 volts, which is characteristic of 3-phenylphthalide, is obtained in practically every case. The cyclic methyl and ethyl esters, apparent exceptions, are reduced at such negative potentials that their wave is combined with that of the resulting 3-phenylphthalide and only one wave with a much higher diffusion current constant than that observed for the other esters is obtained. The formation of such a product from the cyclic derivatives indicates that these compounds are reduced directly to 3-phenylphthalide and ROH (RSH). The normal derivatives on the other hand, must be first reduced to the benzhydrol and then lose ROH (RSH) spontaneously to form 3-phenylphthalide. Further reduction of 3-phenylphthalide probably involves the CO grouping and not the lactone linkage since ethyl benzilate, a vinylog of 3-phenylphthalide, showed no reduction whereas ethyl benzoate can be reduced at the dropping mercury electrode.

Data obtained from the half-wave potentials in buffers I and II indicate that the esters can be divided into two classes. One group which includes the cyclic methyl and ethyl esters is characterized by a stability toward hydrolysis in the more alkaline buffer II, and by half-wave potentials which are independent of *p*H. The stability of this class toward alkali is not surprising since they are ketal-like in structure. A comparison of the half-wave potentials of this group indicates that the ease of reduction increases with increasing ionization constant of the alcohol or phenol concerned. Thus the thiophenyl ester is the easiest to reduce while the reduction of the methyl and ethyl esters becomes more difficult in that order. This behavior is in agreement with the mode of reduction of these compounds to 3-phenylphthalide. This class contains without doubt all the cyclic esters and by coincidence contains the higher melting isomers.

The second class of compounds which contains the normal ethyl and methyl esters is rather irregular in its behavior. The variation of half-wave potentials for the aliphatic esters, ethyl and methyl, with *p*H is similar to that for benzophenone. The shift in value in buffer II, however, may be due to hydrolysis to the acid. The aromatic esters on the other hand are reduced at approximately the same potential of 1.28 volts in both buffers. In the more alkaline buffer II the phenyl ester is slightly hydrolyzed since it gives in addition to the wave at 1.28 volts, a wave with a half-wave potential of 1.53 volts which is characteristic of the acid. The thiophenyl ester gives waves at 1.22, 1.47 and 1.63 volts. The wave at 1.47 volts indicates the probable presence of some of the cyclic derivative. No explanation can be offered for the wave at 1.63 volts. The behavior of this class, provided no interaction has taken place with the buffers, is surprising since due to their structural similarity to benzophenone their half-wave potentials would be expected to vary with *p*H. The similarity in behavior of the isomeric β-naphthol esters as far as the half-wave potentials are concerned is anomalous and is being investigated further. This second class contains all the lower melting esters and must without doubt consist of the normal esters.

The behavior of 2-benzoylbenzoic acid in unbuffered medium, 0.1 *M* tetrabutylammonium iodide–50% dioxane is rather difficult to explain. Neither of the two waves obtained at 1.11 and 1.60 volts, respectively, represents a hydrogen wave since benzoic acid which has approximately the same acidity gives a curve with a half-wave potential of 1.87 volts. The first wave at 1.11 volts no doubt represents a reduction by a mechanism possible only in acid media, the acid being provided by the compound itself. This interpretation is confirmed by results obtained for 2-benzoylbenzoic acid in 0.1 *N* hydrochloric acid, 50% dioxane solution in which a wave with a half-wave potential of 0.95 volt was obtained. After 50% of the acid is reduced in the 0.1 *M* tetrabutylammonium iodide, 50% dioxane solution, the solution around the drop is no longer acid and a second type of reduction occurs.

The nature of this reduction is not clear but it may possibly be a reduction of the pseudo acid. This same type of reduction appears with some of the anhydrides. In buffered media where the acid is present as an anion, the ion must exist in the open form since the half-wave potential changes with *p*H. Such a behavior is in agreement with absorption spectra data obtained in dilute alkali.[2]

No definite structures can be assigned to the anhydrides due to the fact that they are hydrolyzed or interact with the more alkaline buffer II. The mixed acetic anhydride is largely hydrolyzed in both buffers, and gives a reduction wave characteristic of the 2-benzoylbenzoate ion. The anhydride and 3,3'-diphenyldiphthalyl sulfide are apparently stable in buffer I. The approximately equal reduction potentials observed for these two compounds in buffer I would suggest similar structures provided no interaction has occurred with the buffer.

Experimental

The current-voltage curves were determined with a Model XI, Heyrovsky Polarograph having a current scale calibrated in microamperes. Curves for anthraquinone in buffer I and II were obtained with a Fisher Elecdropode. No changes in anode potential with increasing potential was observed with either of these buffers.

The electrolysis cell had a simple cylindrical shape with a mercury pool anode and was provided with side arms for anode connections and for admission of nitrogen for the removal of dissolved oxygen. Anode potentials were measured against a saturated calomel electrode (S. C. E.) by using a sintered glass salt bridge of the type described by Laitinen.[7]

The dropping mercury electrode had the following characteristics. At a pressure of 46.5 cm. of mercury, the drop time in the solvent used was 3.34 seconds (open circuit). The value of *m* was 2.05 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 1.973 mg.$^{2/3}$ sec.$^{-1/2}$.

Materials.—The solutions used had the following compositions and anode potentials: 0.1 *M* tetrabutylammonium iodide,[8] 50% dioxane, anode potential, −0.400 volt; 0.1 *M* hydrochloric acid, 50% dioxane, anode potential, −0.249 volt.

Buffer I.—A mixture which was 0.172 *M* in tetramethylammonium hydroxide, 0.1 *M* in tetramethylammonium iodide, 0.102 *M* in phosphoric acid and 50% dioxane by volume, anode potential, −0.390 volt.

Buffer II.—A mixture which was 0.196 *M* in tetramethylammonium hydroxide, 0.10 *M* in tetramethylammonium iodide, 0.092 *M* in phosphoric acid and 50% dioxane by volume, anode potential, −0.382 volt.

2-Benzoylbenzoic acid, benzophenone, benzoic acid, ethyl benzoate and anthraquinone were obtained from stock. The aromatic esters,[5a,9] 3-phenylphthalide,[10] 4'-hydroxydiphenylphthalide,[11] anhydrides,[12] 3,3'-diphenyldiphthalyl sulfide,[13] methyl,[4] and ethyl esters[3] were prepared by appropriate methods given in the literature.

Summary

The polarographic method is a suitable means of distinguishing between the cyclic and normal esters of 2-benzoylbenzoic acid.

The anhydrides of 2-benzoylbenzoic acid cannot be assigned structures with certainty since they hydrolyze in more alkaline solutions.

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(9) The authors wish to thank Dr. F. F. Blicke for small amounts of the isomeric thiophenyl and B-naphthyl esters which were used for mixed melting points with the compounds prepared for this study.

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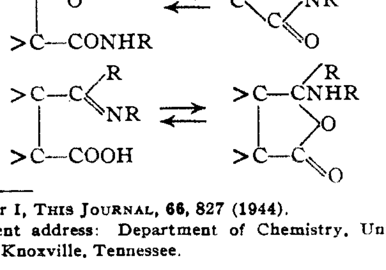
Knoxville, Tenn. Received January 31, 1944

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Behavior of γ-Keto- and Aldehydo-Acid Derivatives at the Dropping Mercury Electrode. II. Amides of 2-Benzoylbenzoic Acid[1]

By S. Wawzonek,[2] H. A. Laitinen and S. J. Kwiatkowski

Amides of γ-keto- and aldehydo-acids can exist in two isomeric forms and can exhibit ring-chain tautomerism of the types



Chemical evidence can indicate what type of ring-chain tautomerism exists or is possible but does not as a rule denote which form is the predominant one.

In this paper the use of the polarograph as a means of ascertaining the type and the approximate amount of ring-chain tautomerism present with amides of 2-benzoylbenzoic acid will be presented.

Results

The behavior of various amides of 2-benzoylbenzoic acid and their derivatives was studied in both unbuffered and buffered media. A summary of the observed half-wave potentials and individual diffusion current constants in the various solutions is given in Table I.

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(1) Paper I, This Journal, **66**, 827 (1944).

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