hour the color of permanganate is apparent; if, however, a drop of silver nitrate solution is added after the two solutions are mixed the color of permanganate appears immediately. The color of a solution of chromic and cobaltic salts appears after twenty-four hours to have changed little, if any, from the greenish blue of the cobaltic ion; if a drop of silver nitrate is then added the color soon becomes a yellowish-green and after half an hour the color is almost that of pure dichromate.

Summary

Measurements have been described above of the electromotive force of the system comprising as one half-cell a gold electrode immersed in a solution of cobaltous and cobaltic nitrates in 1 to 4 *f* nitric acid, and as the other half-cell a hydrogen electrode in 1 or 2 *f* perchloric acid. Conditions for the attainment of reproducible potentials have been discussed. The formal oxidation potential for the reaction $Co^{III} + E^{-I} = Co^{II}$ has been computed to have values at 0° ranging from **1.800** volts in 1 *f* nitric acid to **1.816** volts in 4 *f* nitric acid, and values at 25° of **1.842** volts in 3 *f* acid and **1.850** volts in 4 *f* acid. Values of the decrease in free energy and heat content for the reaction have also been presented.

A brief discussion of the rate of reduction of cobaltic salts by water in nitric acid solution in the presence of silver nitrate has been given.

PASADENA, CALIF. RECEIVED APRIL 26, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Dipole Moments of Hydrazides

BY PAUL R. FREY[1] AND E. C. GILBERT

On the basis of a postulated unbalanced electronic structure for hydrazine it was predicted a number of years ago by Stieglitz that certain types of hydrazine derivatives should undergo rearrangement of the so-called Stieglitz–Lossen type. The correctness of this prediction has been demonstrated by Stieglitz and his students[2] and by independent work in this Laboratory.[3]

In the earlier work[2] it was proved that benzoyl hydrazide, *sym*-dibenzoyl hydrazide, and azodibenzoyl undergo rearrangement, and in the later work α-benzoyl-β-*p*-chlorobenzoyl hydrazide, α-benzoyl-β-*p*-toluyl hydrazide and α-benzoyl-β-*p*-nitrobenzoyl hydrazide were found to react similarly. In the case of the unsymmetrical derivatives the products of the reaction seemed definitely to indicate that substituents in the benzoyl group affect the electronic charge on the nitrogens, rendering one or the other more "positive" depending upon the substituent.

Recently the dipole moments of hydrazine and a number of its simple derivatives have been measured[4] and molecular structure calculated from quantum mechanical considerations.[5] These measurements confirm the correctness of the early postulate that hydrazine and its derivatives possess an unbalanced electronic configuration. Furthermore, the ingenious shift in molecular orientation used by Ulich, Peisker and Audrieth[4] to explain their dipole measurements for substituted hydrazines seems to offer a possible explanation for the results obtained in rearrangements in this Laboratory.[3]

The present work was begun before the supporting results of the other investigators were available.[4,5] It had for its purpose a study of the dipole moments of those hydrazides which were known to undergo rearrangement in the hope of finding some fundamental explanation for their behavior. The experimental work presented considerable difficulty because of the relative insolubility of the compounds in non-polar solvents, necessitating special care and the use of somewhat lower concentrations than those usually employed.

Experimental Part

Apparatus.—The heterodyne beat method[6] was used to measure dielectric constants. The two oscillators employed type 112-A tubes as a source of oscillation and were coupled to a three-tube resistance-coupled amplifier using

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[1] This paper is taken in part from the Ph.D. dissertation of Paul R. Frey, Oregon State College, June, 1936.

[2] Stieglitz and Senior, THIS JOURNAL, **38**, 2727 (1916); Stieglitz and Brown, *ibid.*, **44**, 1270 (1922); Gilbert, Abstract of Theses, University of Chicago, Science Series, **1**, 177 (1923).

[3] Gilbert, THIS JOURNAL, **49**, 286 (1927).

[4] Audrieth, Nespital and Ulich, *ibid.*, **55**, 673 (1933); Ulich, Peisker and Audrieth, *Ber.*, **68B**, 1677 (1935).

[5] Penney and Sutherland, *Trans. Faraday Soc.*, **30**, 898 (1934).

[6] Williams, THIS JOURNAL, **52**, 1831 (1930).

type 40 hi-mu tubes in the first two stages and a type 71-A tube in the output stage. The output from the 71-A tube was fed into a thousand cycle electrically driven tuning fork which in turn was connected to a radio loudspeaker of the vibrating diaphragm type. The two oscillators were placed twenty-five feet (7.6 meters) apart with the coils at right angles. The frequency of one oscillator was fixed at 1000 kilocycles by means of a Bliley X-cut quartz crystal. The frequency of the other was controlled by means of a type 222-L General Radio precision condenser of 1500 $\mu\mu$f maximum capacity in series with a fixed mica condenser of 271.0 $\mu\mu$f capacity, calibrated in terms of the precision condenser.

The dielectric cell was constructed from a vernier type of radio air condenser, the brass parts of which were gold plated. The movable plates were provided with stops which permitted the condenser to be set at maximum and minimum capacity only. The cell had a capacity of 23.87 $\mu\mu$f.

In the calibration of the fixed mica condenser in series with the precision condenser, the dielectric cell, and in all subsequent measurements of the capacitance by the substitution method, the same initial readings of the precision condenser were used. The balance for zero beats was obtained by means of the variable air condenser in the oscillator unit. This procedure eliminated duplicate calculations of the capacity of condensers in series, and errors due to a slight variation in the capacity of the precision condenser compared to that obtained by interpolation from the calibration chart accompanying the instrument.

Materials.—Benzene was purified with all the usual precautions and had the constants: m. p. 5.4°; b. p. 80.4°; $\epsilon = 2.273$ at 25°; d^{25}_4 0.87361; n^{25}_D 1.49781.

Dioxane consisted of Eastman best grade, purified, and had the constants: $\epsilon = 2.3051$ at 25°; d^{25}_4 1.02687; n^{25}_D 1.42025. These constants agree very well with those found by Smyth[7] but differ somewhat from others. In fact scarcely any two observers so far have reported the same dielectric constant for this compound. The same sample was used throughout all our work.

Benzoyl hydrazide was prepared by the action of hydrazine hydrate on methyl benzoate and purified by repeated recrystallization from water. The m. p. was 112°.

Dibenzoyl hydrazide was prepared by the action of hydrazine sulfate on benzoyl chloride in alkaline solution and recrystallized from water. It melted at 238°.

Azodibenzoyl was prepared from the sodium salt of dibenzoyl hydrazide. This was converted to the mercury salt by addition of mercuric chloride in alcohol. The mercuric salt which precipitated was washed repeatedly, dried, and then treated with bromine in dry ether. Excess bromine was removed by shaking with mercury. Azodibenzoyl crystallized out upon evaporation of the ether, and was thrice further recrystallized from dry ether, m. p. 118°. α-Benzoyl-β-*p*-toluyl hydrazide, m. p. 220°, α-benzoyl-β-*p*-chlorobenzoyl hydrazide, m. p. 222°, and α-benzoyl-β-*p*-nitrobenzoyl hydrazide, m. p. 239°, were prepared and purified in the manner previously described.[3]

2,5-Diphenylfurazan (also called in older literature diphenylfurodiazol), a ring compound resulting in considerable amount from the rearrangement of the dibenzoyl hydrazide, was available and its dipole moment was measured, though it is not of primary interest, m. p. 140°.

Benzene was used as solvent for benzoyl hydrazide, azodibenzoyl, and 2,5-diphenylfurazan, and dioxane for all others. All measurements were made at 25°. All weighings were corrected to vacuum. Refractive indices were measured with a Bausch and Lomb dipping refractometer.

Cryoscopic determination was made of the molecular weights of the various compounds in benzene. In no case was there any evidence of association. It was feared that reaction might occur between the hydrazides and dioxane. Samples were allowed to stand for some time at elevated temperatures in dioxane. Upon evaporation of the dioxane, the melting points of the hydrazides were unchanged.

Results

The values of P_∞ (P_2 extrapolated to zero concentration) were obtained from the ordinary equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{N_1M_1 + N_2M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{N_2} + P_1$$

Values of μ were calculated from the Debye equation

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - P_{(E+A)})\,T} \text{ e. s. u.}$$

P_A was assumed to be 15% of P_E.

In Table I are given the results for the seven compounds investigated.

Discussion

Measurements in the more dilute solutions revealed the presence of a phenomenon observed by others who have attempted work under similar conditions,[8] namely, very high dilution. When P_2 is plotted against N_2 the curve is rectilinear at higher concentrations but, although it is smooth, it develops a decided curvature as the concentration approaches zero. Various attempts have been made to explain it. It is noteworthy that the same type of curvature was observed in both solvents by us so it was presumably not a solvent effect, and the cryoscopic measurements did not indicate association of the solute. This effect leads to ambiguity in the choice of P_∞ since P_∞ may be taken from a straight line extrapolation from points of higher concentration or by extrapolation from values in the most dilute solutions. We were interested primarily in the dipole moment as conventionally determined, hence values of P_∞ were taken from the straight line extrapolation as a basis for calculation. Azodibenzoyl and diphenylfurazan exhibited the highest solu-

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(7) Smyth, THIS JOURNAL, **53**, 2116 (1931).

(8) (a) Svirbely, Ablard and Warner, *ibid.*, **57**, 652 (1935); (b) Earp and Glasstone, *J. Chem. Soc.*, 1709 (1935); (c) Geddes and Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936).

bility and their curves were used as a basis for establishing the proper extrapolation in the case of the dibenzoyl and nitrobenzoyl compounds.

TABLE I

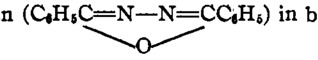
N_2	ϵ	d^{25}_4	n^{25}_D	P_2
Benzoyl hydrazide ($C_6H_5CONHNH_2$) in benzene				
0.000000	2.2730	0.87361	1.49781	...
.000311	2.2776	.87379	1.49789	242
.000579	2.2811	.87401	1.49794	229
.000864	2.2840	.87416	1.49800	212
.001121	2.2870	.87431	1.49805	210
.001435	2.2903	.87449	1.49811	204
Azodibenzoyl ($C_6H_5CON{=}NCOC_6H_5$) in benzene				
0.000544	2.2807	0.87387	1.49792	287
.000872	2.2860	.87419	1.49803	278
.001684	2.2958	.87475	1.49819	258
.003381	2.3167	.87597	1.49861	248
.005952	2.3488	.87786	1.49907	244
.009051	2.3864	.88011	1.49976	240
.012713	2.4323	.88268	1.50060	239
2,5-Diphenylfurazan  $(C_6H_5\underbrace{C{=}N{-}N{=}C}_{O}C_6H_5)$ in benzene				
0.000869	2.2920	0.87418	1.49809	373
.001213	2.2983	.87458	1.49821	354
.001547	2.3033	.87479	1.49832	338
.001956	2.3104	.87507	1.49843	331
.002499	2.3208	.87550	1.49864	323
.003335	2.3356	.87613	1.49889	324
α,β-Dibenzoyl hydrazide ($C_6H_5CONHNHCOC_6H_5$) in dioxane				
0.000000	2.3051	1.02687	1.42025	...
.000331	2.3105	1.02700	1.42038	286
.000491	2.3126	1.02711	1.42045	270
.000808	2.3169	1.02731	1.42061	259
.001105	2.3198	1.02745	1.42069	242
α-Benzoyl β-*p*-toluyl hydrazide ($C_6H_5CONHNHCOC_6H_4CH_3$) in dioxane				
0.000438	2.3153	1.02703	1.42052	387
.000793	2.3222	1.02721	1.42068	363
.001034	2.3269	1.02737	1.42086	354
.001469	2.3350	1.02756	1.42106	344
.001871	2.3423	1.02781	1.42128	337
α-Benzoyl β-*p*-chlorobenzoyl hydrazide ($C_6H_5CONHNHCOC_6H_4Cl$) in dioxane				
0.000489	2.3236	1.02723	1.42054	456
.000943	2.3306	1.02755	1.42083	435
.001268	2.3381	1.02780	1.42104	421
.001773	2.3493	1.02812	1.42130	407
.002211	2.3602	1.02844	1.42152	405
α-Benzoyl β-*p*-nitrobenzoyl hydrazide ($C_6H_5CONHNHCOC_6H_4NO_2$) in dioxane				
0.000553	2.3370	1.02729	1.42057	858
.000879	2.3532	1.02760	1.42078	815
.001216	2.3688	1.02788	1.42098	781
.001558	2.3845	1.02819	1.42121	758
.001947	2.4026	1.02856	1.42146	744

TABLE II

Substance	P_∞	P_E	μ
Benzoyl hydrazide	192	36	2.70
Dibenzoyl hydrazide	220	66	2.63
Benz.-toluyl hydrazide	328	78	3.38
Benz.-chlorobenz. hydrazide	394	79	3.82
Benz.-nitrobenz. hydrazide	736	80	5.57
Azodibenzoyl	247	68	2.85
Diphenylfurazan	325	66	3.45

Some of the work embodying similar results in dilute solution[8a] has been criticized adversely[9] but the criticism extended even to the values in more concentrated solutions. It is nevertheless believed that the results presented here represent reliable experimental values. This is supported by the fact that the values for the solvents themselves are those found by absolute measurements with the apparatus and not those taken from the literature and assumed to be correct.

The moments of the hydrazides as found are of interest, since they seem at first thought to be lower than might be expected. For instance the moment for benzamide is approximately 3.6 while that for benzoyl hydrazide is much less—2.7. (All dipole moments in this paper are expressed in Debye units, 1×10^{-18}.) On the other hand, the moment of the *sym*-dibenzoyl compound is only very slightly less than that of the unsymmetrical monobenzoyl hydrazide. The complexity of these compounds makes quantitative calculations of the moment from a postulated structure of little ultimate value and such will be omitted here. Qualitative calculations made alternatively on the basis of their structure as derivatives of hydrazine, of benzoic acid, or of benzamide show very reasonable agreement with the experimental results. In making these calculations it is necessary to assume for the substituted hydrazides, as was done for hydrazines by Ulich, Peisker, and Audrieth,[4] that variation of the substituent group causes a shift in the space configuration of the molecule. They applied this theory to hydrazines, where the phenyl group is directly attached to the nitrogen, with considerable success. The net result seems to be that regardless of the sign of the moment of the substituent it is *added* vectorially, due to the two optional positions which it may assume in the unsymmetrical hydrazine molecule. This agrees with the fact observed in the rearrangements of the hydrazides[3] that different substituents apparently af-

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[9] Bergmann and Weizmann, THIS JOURNAL, **57**, 1755 (1935).

fect the electronic configuration of the nitrogen atoms or at least stand in different relation to them.

The high moment of azodibenzoyl indicates that this compound cannot have a simple *trans* form as is found in azobenzene. This is in line with the observation that benzalazin[4] likewise possesses a moment, intermediate between that of azobenzene and azodibenzoyl.

Summary

The dipole moments of a series of seven hydrazides and related derivatives have been determined and discussed.

CORVALLIS, OREGON RECEIVED MARCH 29, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ALBERTA]

The Binary Systems of Some Fatty Acids[1]

BY M. KULKA AND R. B. SANDIN

A number of investigators working on binary systems formed by even-numbered fatty acids have come to the conclusion that there is definite compound formation, usually of the type 1 mole A:1 mole B. Probably the best example of this is the case of palmitic and stearic acids. This system has been investigated by de Visser[2] and by Shriner, Fulton and Burks.[3] De Visser concluded that mixed crystals were formed in the vicinity of the 50% mixture, whereas Shriner and his co-workers have concluded that their curve indicates compound formation. In this connection it should be pointed out that Slagle and Ott,[4] doing work on X-ray studies of mixtures of fatty acids, have come to the conclusion that the existence of a transition point for mixtures of palmitic and stearic acids may indicate a change in modification only.[5] Whatever conclusions we come to, as a result of all the work recorded up to the present time, this fact stands out, *viz.*, that the already determined melting point curves of binary systems of even-numbered fatty acids and differing by two carbon atoms, are all very similar. There are always two inflections in each curve. One inflection is very close to the equimolecular mixture of the two acids and indicates compound formation to many workers. The second inflection occurs very close to the mixture which contains 0.725 mole per cent. of the lower melting acid. This point corresponds to the eutectic temperature.

Very recently Smith[6] working with "odd-even" acid systems has shown two definite changes in the direction of the curve for the binary system, margaric acid–stearic acid. Again these two points correspond very closely to the two points of inflection recorded for binary systems of even-numbered fatty acids. According to Smith "it seemed unlikely that the covalency forces would differ sufficiently to prevent compound formation between 'odd' and 'even' acids."

The purpose of the present investigation was to extend the information on the binary systems of fatty acids. Three systems which do not seem to be recorded in the literature were investigated, *viz.*, palmitic–myristic, lauric–capric and lauric–undecylic. The first two systems will complete the series of recorded ones (systems of even-numbered fatty acids and differing by two carbon atoms) from *n*-eicosanic acid to capric acid. The third system studied adds another example to the type investigated by Smith,[6] *viz.*, margaric acid–stearic acid.

Experimental

Fatty Acids.—Eastman fatty acids were recrystallized repeatedly from acetone until constant capillary tube melting points were obtained, *viz.*: palmitic acid, m. p. 62.6–62.9°; myristic acid, m. p. 54.5–54.8°; lauric acid, m. p. 43.9–44.1°; capric acid, m. p. 31.3–31.8°; undecylic acid, m. p. 28.8–29.2°.

Determination of Freezing Points.—The freezing points of the mixtures were determined in the apparatus similar to that used for determination of molecular weights by the freezing point method. The temperature of the outside bath was maintained 3° below the freezing point of the particular mixture used. The degree of supercooling allowed

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(1) Abstracted in part from a thesis submitted by M. Kulka to the Graduate School of the University of Alberta for the degree of Master of Science.

(2) De Visser, *Rec. trav. chim.*, **17**, 182 (1898).

(3) Shriner, Fulton and Burks, THIS JOURNAL, **55**, 1494 (1933).

(4) Slagle and Ott, *ibid.*, **55**, 4404 (1933).

(5) The authors call attention to the work done on binary systems of even-numbered fatty acids by Morgan and Bowen [*J. Soc. Chem. Ind.*, **43**, 346 (1924)]; Bhatt, Watson and Patel [*J. Indian Inst. Sci.*, **13A**, Pt. 11, 141 (1930)]; and Piper, Chibnall and Williams [*Biochem. J.*, **28**, 2182 (1934)].

(6) Smith, *J. Chem. Soc.*, 625 (1936).