effect detracts from its usefulness as an oxidation–reduction indicator. Accordingly the chief interest in this investigation lies in the discovery that thioindigo disulfonate undergoes dimolecular reduction. Since in the range of acidity investigated there were no signs of a second step of reduction, and since the E_0'–pH curve for hydrogen does not parallel that for the dye, it seems improbable that we are dealing with a meriquinone. Moreover, meriquinones would presumably be deeply colored while our compound is yellow. The mathematical formulation rules out the possibility of a semiquinone. As far as we are aware this is the first case of a thermodynamically reversible dimolecular oxidation–reduction reaction reported in the literature. The discovery has added interest because it has commonly been assumed that the leuco compounds of thioindigo and its derivatives have structures similar to indigo white. We are not yet prepared to hazard a guess as to the structure of the leuco compound. Work is now in progress in this Laboratory in an attempt to answer this question.

Summary

1. The reduction potentials of the system thioindigo disulfonate–leuco compound have been measured from pH 2.02 to 7.61 and at 12.59.

2. The potentials were found to be a linear function of the concentration of the oxidant at constant percentage oxidation.

3. In all cases except in strongly alkaline solution the results were shown to conform to the thermodynamic equations developed for a one step dimolecular reduction involving one electron per molecule of dye. In alkaline solution also the reduction is dimolecular.

DETROIT, MICH. RECEIVED MARCH 7, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Organic Deuterium Compounds. Acetic, Malonic and Succinic Acids

BY J. O. HALFORD AND LEIGH C. ANDERSON

Two methods of approach are available for the synthesis of organic compounds containing deuterium. The first, the direct transfer by means of the exchange reaction, has been used, for example, in the preparation of benzene-d_6.[1] It has the obvious disadvantage of requiring the depletion, in deuterium, of relatively large quantities of heavy water, and of making the removal of the last traces of ordinary hydrogen very difficult. The second method is the direct hydrolysis, hydrogenation or hydration of appropriate carbon compounds. Examples of this type of approach are the preparation of acetylene-d_2[2] and of methane-d_4[3] by the hydrolysis of metallic carbides, and the hydration of carbon suboxide to malonic-d_2 acid-d_2[4] as shown by the equation

$$C_3O_2 + 2D_2O \longrightarrow CD_2(COOD)_2$$

When Wilson's description of malonic-d_2 acid-d_2 and of acetic-d_3 acid-d appeared, the present authors had been studying the synthesis of these acids by the same method and had samples of both substances available, although the details of the method had not yet been worked out in an entirely satisfactory manner. Wilson's excellent procedure leaves nothing to add, except that the use of a benzene solution of carbon suboxide, rather than the pure liquid, may not be necessary.

The present contribution is concerned with these acids, together with acetic acid-d,[5] acetic-d_3 acid, and three new succinic acids. Melting points of the seven compounds are compared with those of the respective "parent" substances and measurements of the vapor pressures of the several acetic acids are presented.

The preparation of succinic-d_4 acid-d_2 employed the reduction of potassium acetylene dicarboxylate by means of a dilute sodium amalgam and deuterium oxide

$$C_2(COO)_2^{--} + 4Na + 4D_2O = (CD_2COO)_2^{--} + 4Na^+ + 4OD^-$$

followed by acidification with DBr in D_2O

$$(CD_2COO)_2^{--} + 2D^+ = (CD_2COOD)_2$$

Succinic-d_4 acid and succinic acid-d_2 were prepared by treating succinic-d_4 acid-d_2 and succinic acid, respectively, with water and deuterium

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(1) Bowman, Benedict and Taylor, THIS JOURNAL, **57**, 960 (1935).

(2) Clemo and McQuillen, *J. Chem. Soc.*, 851 (1935); Herzberg, Putat and Spinks, *Nature*, **33**, 951 (1934).

(3) Urey and Price, *J. Chem. Phys.*, **2**, 300 (1934).

(4) Wilson, *J. Chem. Soc.*, 492 (1935).

(5) Lewis and Schutz, THIS JOURNAL, **56**, 493 (1934).

oxide. The similar behavior of acetic acid, in which only the carboxyl hydrogen is replaced by exchange, is discussed by Lewis and Schutz. The attempt to prepare the corresponding malonic acids of intermediate deuterium content by the same procedure led to the interesting result that all four of the hydrogen atoms of malonic acid are replaced, apparently rapidly and without the conscious introduction of a catalyst, by direct exchange with deuterium oxide.

Easy replacement of the methylene hydrogens makes it possible to prepare malonic-d_2 acid-d_2 rapidly by direct reaction with deuterium oxide, subject, of course, to the inefficiency of the method. In this case, the required depletion of deuterium oxide is probably no more troublesome than the alternative preparation of carbon suboxide, although the latter method is better if complete replacement by deuterium is desired. A quantitative study of the exchange reaction, using dilute deuterium oxide, is now under way in this Laboratory.

Thus far, the observed differences between the melting points of corresponding hydrogen and deuterium compounds are relatively small,[6] reaching a maximum with water, or possibly with benzene, if the recently reported melting point of benzene-d_6 is correct. As an example, it may not be out of place to mention here our experience with triphenylmethane-*d*, to show how small the effect of replacement in a large molecule may be. This compound, prepared by the reaction of triphenylbromomethane with deuterium iodide in deuterium oxide, showed a melting point and an ultraviolet absorption spectrum indistinguishable from triphenylmethane. The melting points of the acids discussed in this paper are presented in Table I.

TABLE I

Acid	M. p., °C.	Notes
Malonic-d_2 acid-d_2	130–131	Wilson reports 128–130
Malonic acid	133–134	Control from C_3O_2 and H_2O
Acetic acid-*d*	15.4	Lewis and Schutz report 13.3
Acetic-d_3 acid	17.2	
Acetic-d_3 acid-*d*	15.8–16	Wilson reports 15.8
Acetic acid	16.7	Control from control malonic acid
Succinic acid-d_2	179–180	
Succinic-d_4 acid	181–182.6	
Succinic-d_4 acid-d_2	178–179.1	
Succinic acid	182.7–183.2	Control made from potassium acetylene dicarboxylate

The dependence of the melting point upon the number and position of the deuterium atoms is quite regular. The substitution by deuterium of the carboxyl hydrogen of acetic acid or acetic-d_3 acid produces a lowering of 1.3°, and the substitution of the three methyl hydrogens of acetic acid or acetic acid-*d* results in an increase of 0.5°. Thus the difference, 0.8°, between acetic acid and the completely substituted acetic-d_3 acid-*d* may be looked upon as the result of the operation of two effects of opposite sign. A similar regularity appears with the succinic acids, but here the highest melting point is exhibited by ordinary succinic acid, so that the effect of substitution anywhere in the molecule is to produce a decrease. For the carboxyl groups, the decrease is about 3°, and for the four hydrogens attached to carbon, about 1°. The magnitude of the difference with malonic-d_2 acid-d_2 suggests effects similar in sign to those exhibited by succinic acid, although the point could not be established without malonic acids of intermediate deuterium content.

It is evident that a number of factors must be considered as contributing to the melting point differences recorded here and elsewhere. The complexity of the problem may be illustrated by the following points, which are outlined as a tentative basis for classification of the effects.

1. The formation of a complete series of solid solutions indicates similarity of crystal structure. The heavier substance should show closer packing along with lower intermolecular vibration frequencies, resulting in a higher energy of sublimation or melting, and tending consequently toward an elevation of the melting point. The magnitude of the increase should be greater for greater mass differences, and should decrease at higher temperatures as the higher vibrational states come into play. The effect at any one temperature would be greater for small molecules than large ones, for a like reason.

2. The introduction of rotational energy as the molecule is released from the crystal is the same for the heavy and light substances. The accompanying entropy change will favor the formation of the heavier liquid and tend toward a lower melting point.

3. Association in the liquid may be greater (acetic acid-*d*) or less (D_2O) for the heavy com-

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[6] Benzene, naphthalene, Clemo and McQuillen, *J. Chem. Soc.*, 851, 1325 (1935); DI and DBr, Bates, Halford, and Anderson, *J. Chem. Phys.*, **3**, 415, 531 (1935); DCN, Lewis and Schutz, THIS JOURNAL, **56**, 1002 (1934).

pound. This has been discussed by Lewis and Schutz and by Wilson. Other things being equal, higher association produces a lower melting point, as can be seen readily by considering imaginary equilibria between a solid and two liquid forms, respectively, of different degree of association.

Factors 1 and 3 are more important, relative to factor 2, at lower temperatures, while factor 2 is relatively independent of the temperature.

It is suggested that acetic-d_3 acid melts above acetic acid because of the predominance of factor 1 and the absence of factor 3 (since ordinary carboxyl groups are present in both acids). Factor 3 is concerned almost exclusively in the comparison of acetic acid-d with acetic acid. Succinic-d_4 acid melts below succinic acid because at the higher temperatures and with the more complex molecule, factor 1 is of less importance, and factor 2 predominates.

The melting points of the hydrogen halides can be interpreted by the above scheme. The reversal observed in going from the iodides to the chlorides involves the sensitivity of factor 1 to temperature and relative mass, while the fluorides fal out of line because of factor 3, which operates in the same manner as with the acetic acids.

TABLE II

Temp., °C.	Δp (mm. Hg) CD_3COOD(W)	CD_3COOD	CD_3COOH	CH_3COOD
21.0	0.74	0.55	−0.15	0.11
35.8	1.56	.88	+ .33	.46
41.7	2.07	1.29	.63	.70
48.6	2.85	1.84	1.32	1.34
54.6	3.74	2.35	1.73	1.89
59.7	4.65	2.75	2.57	2.64
65.9	6.03	3.43	3.23	3.69
74.3	8.30	4.69	5.16	5.39
83.6	11.80	6.50	7.76	7.93

The vapor pressures of the acetic acids at temperatures from 20 to 84° are summarized in Table II. The increase over the vapor pressure of acetic acid is given for several temperatures. The first column of pressures, marked in the tabulation CD_3COOD(W), was obtained by interpolation from Wilson's measurements.

The data for acetic acid-d are not in agreement with those of Lewis and Schutz.[5] The values presented for each acid were obtained in the second of two sets of measurements. After the first data had been obtained, the acid was redistilled and the measurement was repeated using the middle fraction consisting of about half the original liquid. No significant change in the vapor pressures of acetic acid-d and acetic-d_3 acid was produced by the distillation, but acetic-d_3 acid-d showed an increase over the entire temperature range. The data for this acid are therefore less reliable than for the others. Further distillation would tend toward values in the direction of Wilson's data, but would probably not account for the entire difference.

It may be concluded that the substitution of the three methyl hydrogens by deuterium produces an elevation of the vapor pressure of about the same magnitude as the effect produced by the corresponding substitution of the carboxyl hydrogen. The differences recorded at the lowest temperature are too small to allow significance for the one negative difference observed. It is interesting, however, that the negative difference was found for the one acid which shows a higher melting point than ordinary acetic acid. The total vapor pressures are in all cases very close to the same value.

The purity of the malonic and succinic acids is shown by the molecular weights given in Table III. The data were obtained by titration with sodium hydroxide to an end-point with phenolphthalein.

TABLE III

Acid	Mol. wt. Found		Calcd.	Notes
Succinic acid-d_2	119.99	120.02	120.06	From succinic acid + D_2O
Succinic-d_4 acid	122.02	122.00	122.07	Succinic-d_4 acid-d_2 + H_2O
Succinic-d_4 acid-d_2	123.95	123.97	124.08	From $K_2C_4O_4$
Malonic-d_2 acid-d_2	107.94	108.04	108.03	From C_3O_2 + D_2O
Malonic-d_2 acid-d_2	107.90	107.79	108.03	Malonic acid + D_2O
Malonic acid	104.28	104.33	104.01	Malonic-d_2 acid-d_2 + H_2O

Experimental

A. Preparations

Carbon Suboxide.—The vapors of diacetyltartaric anhydride,[7] obtained by boiling under reduced pressure (15 to 30 mm.), were carried by means of dry nitrogen into contact with a platinum filament kept at a dull red heat, to form carbon suboxide by thermal decomposition. The impurities, acetic acid, carbon dioxide and possibly also ketene, were removed by fractional condensation and

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[7] Ott and Schmidt, *Ber.*, **55**, 2126 (1922).

distillation. The last distillation was carried out at atmospheric pressure, with the carbon suboxide boiling at 7°. Yields were low, possibly because of excess heating by the filament. The method of Hurd and Pilgrim, as used by Wilson, is probably to be preferred.

Malonic-d_2 Acid-d_2.—Only the preliminary experiments are described, since the work was discontinued upon the appearance of Wilson's paper. Carbon suboxide was distilled at about 300 mm. pressure back and forth through about twice the calculated quantity of 99.6% deuterium oxide in a U-tube until it could be seen to have all reacted. Residual pressure was negligible. A slight amount of polymerization occurred in unpredictable fashion on the walls of the apparatus. We confirm Wilson's observation that contact with excess water prevents polymerization. Excess water was evaporated *in vacuo* at 25–70°, and the product kept in an evacuated desiccator over magnesium perchlorate trihydrate. Seven grams of the acid was prepared in this manner. A portion recrystallized from benzene and "anhydrous" ether in a Soxhlet extractor showed a decrease of molecular weight to 107.2. When treated with two successive small portions of deuterium oxide the mol. wt. increased to 108.0.

One gram of ordinary malonic acid was dissolved in 1.0 cc. of deuterium oxide, and crystallized out by evaporation. A repetition, using 1.0 cc. of deuterium oxide, produced malonic-d_2 acid-d_2 of molecular weight 107.8. The reverse experiment was performed, converting malonic-d_2 acid-d_2 to malonic acid.

Acetic-d_3 Acid-d.—Three grams of malonic-d_2 acid-d_2 was introduced into a small glass apparatus, dried by evacuation, decomposed at 150° under atmospheric pressure, and the resulting acetic-d_3 acid-d distilled first at atmospheric pressure and later in a closed system under its own pressure.

Acetic-d_3 Acid.—The carboxyl deuterium of acetic-d_3 acid-d was replaced by hydrogen by passing dry hydrogen chloride through the liquid, the temperature being kept low to increase solubility and minimize evaporation loss. The evaporation was checked by means of a cold trap, and found to be very slight. The process was tested from time to time by means of the melting point, care being taken first to pump off the hydrogen chloride; it was discontinued when no further increase in the melting point was observed.

Acetic Acid-d.—Freshly dehydrated potassium acetate was treated with concd. D_2SO_4 (in D_2O). The acetic acid-d thus produced was purified by several fractional distillations. The D_2SO_4 solution, obtained by hydrating SO_3 with heavy water, had a sp. gr. of 1.873 ± 0.006. About 2 cc. of acetic acid-d was prepared.

Succinic-d_4 Acid-d_2.—Potassium acetylene dicarboxylate was prepared by treating dibromosuccinic acid with potassium hydroxide in methyl alcohol, as described by Ruggli.[8] It proved convenient to use the resulting mixture of potassium bromide and potassium acetylene dicarboxylate, since attempts to obtain the latter salt in a pure state were attended by polymerization and decomposition. The weight of the dried salt mixture was 96% of the theoretical.

Fourteen grams of mixed salts (0.021 mole $K_2C_4O_4$) was partially dissolved in 15 cc. of 99.6% D_2O. To this was added, in portions, with cooling and stirring, 2 g. of sodium dissolved in 20 cc. of mercury. The mixture was stirred mechanically for one hour. The aqueous layer was separated from the mercury and acidified to a deep blue on Congo Red paper by means of 13.5 cc. of a 50% solution of DBr in D_2O. The DBr solution, freshly prepared by dissolving liquid DBr in D_2O, was free from visible traces of bromine. The mixture of solids and solution was transferred to a 50-cc. flask, in which crystallization and drying were effected by evaporation *in vacuo*, the heavy water being collected in a container cooled with carbon dioxide and acetone. The flask and its solid contents were crushed by means of a metal mortar and pestle, and extracted with "anhydrous" ether in a Soxhlet apparatus. The ether was evaporated and replaced by benzene which was used for washing and filtering the product; yield 2.2 g., 85% of the theoretical based on the $K_2C_4O_4$ + KBr mixture. During the preparation, 28.5 cc. of deuterium oxide was introduced and 28.0 cc. recovered, the difference being approximately correct for the amount of deuterium present in the succinic-d_4 acid-d_2. The product was dissolved in 2.5 cc. of warm D_2O, then recovered and dried by evaporation, in order to replace any deuterium which had been removed during the extraction.

Succinic-d_4 Acid.—0.4 g of succinic-d_4 acid-d_2 was dissolved in 8 cc. of H_2O, then crystallized and dried by evaporation *in vacuo;* yield 0.35 g. **Succinic acid-d_2** was obtained by the corresponding experiment using 1 g. of succinic acid and two successive treatments with 1.0 cc. and 2.0 cc. of D_2O, respectively.

B. Properties

Melting Points.—The acetic acid was distilled into a ten millimeter tube immersed in a cold bath, and allowed to collect as solid near the top of the bath. A water-bath whose temperature could be slowly varied was substituted for the cold bath. The major part of the acid was melted into the bottom of the tube carrying impurities with it. By manipulation of the bath temperature it was found possible to melt and crystallize the acid on the walls within a very narrow temperature range. Thus the melting point of a highly purified sample was obtained although in no case could the melting range for the entire contents of the tube be narrowed to less than 0.5°.

The melting point of each of the deuteriosuccinic acids was obtained with an ordinary unstirred sulfuric acid bath. In order to avoid errors introduced by different rates of heating, each acid was compared directly with ordinary succinic acid immersed in the bath at the same time.

Vapor Pressures.—The difference between the vapor pressure of each of the three deuterioacetic acids and that of a redistilled sample of ordinary acetic acid was measured. The two acids to be compared were sealed into bulbs attached to the two arms of a U tube containing mercury. The mercury was introduced first and heated in a vacuum to remove gases. It was then frozen, the acids were distilled into the evacuated bulbs, frozen in turn by liquid air, and the apparatus sealed off. A second set of measurements was undertaken in order to test the effect of further fractional distillation. The acids in each case were distilled into a new apparatus, then fractionated by distilling

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(8) Ruggli, *Helv. chim. acta*, **3**, 564 (1920).

out approximately 50% of the contents of the bulbs before the apparatus was sealed off.

A partial check upon the reliability of the results was obtained by means of a direct comparison of the reference acetic acid with an acetic acid obtained by the decomposition of malonic acid. A small difference was observed in the first series of measurements but not in the second.

The four pieces of apparatus were immersed in a large water-bath, fitted with a window for observation. The temperature of the bath could be regulated by hand to within ±0.1° at any point in the temperature range. Observations of the mercury levels, corrected for a layer of acetic acid on each mercury surface, were made with a cathetometer, and are probably accurate to better than ±0.1 mm.

Molecular Weights.—Samples weighing about 50 mg. were titrated with 0.05 *N* sodium hydroxide to a phenolphthalein end-point. The volume at the end-point was less than 20 cc. To ensure high accuracy a weight buret was used, carbon dioxide was carefully excluded, and the end-point was observed in the cold with a uniform quantity of indicator. The error of manipulation was of the order of ±0.03%. Any further error, to a total of about ±0.05%, is to be ascribed to the difficulty of uniformly removing the last traces of water from the solids. Since the measurements are comparative, the alkali solution was standardized with the ordinary malonic and succinic acids.

Summary

1. The preparation and melting points of acetic-d_3 acid-d, acetic-d_3 acid, acetic acid-d, malonic-d_2 acid-d_2, succinic-d_4 acid-d_2, succinic acid-d_2 and succinic-d_4 acid are presented and discussed, together with the vapor pressures of the acetic acids.

2. The hydrogens of the methylene group of malonic acid are easily replaced by deuterium when the acid is dissolved in deuterium oxide. The hydrogens of the ethylene group of succinic acid are not replaced under comparable conditions.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 27, 1935

[CONTRIBUTION NO. 39 FROM THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Molecular Weights of Polymeric Substances in Catechol and their Bearing on the Nature of Coal and Derived Products

BY R. C. SMITH AND H. C. HOWARD

Catechol has been found[1] to be an excellent solvent for such primary degradation products of bituminous coal as (a) the "humic acids," prepared by mild oxidation; (b) the "solid bitumens," obtained by solvent action, by distillation in high vacuum, and by mild hydrogenation. Cryoscopic measurements gave freezing point depressions corresponding to average molecular weights ranging from 200 to 300. The physical properties of both the "humic acids" and the "bitumens" indicate that these substances are of high molecular weight, and the observed ΔT for the bitumens in diphenyl, a non-polar solvent, leads to values of molecular weight greater than 1000. The present investigation was undertaken in order to determine whether any well-characterized polymeric solutes would give anomalous values for molecular weight in catechol, and, for purposes of comparison, measurements were also made, wherever solubility permitted, in diphenyl.

Method and Materials.—The semi-micro technique used in determining the molecular weights was similar to that already described,[1] except that a stoppered, side-neck test-tube was used to hold the melt. The stopper carried a Koppers Refined Products 1/10° thermometer, 70–120°, and a small sleeve of copper tubing through which the stem of the ring agitator passed. A slow stream of dry nitrogen was passed into the side tube and escaped through the sleeve around the agitator, thus maintaining an inert atmosphere over the solution at all times. Except when freezing point determinations were being made the air-bath was maintained 10–20° above the melting point and the agitator was run continuously. After several hours some of the solvent sublimed from the melt to the cooler parts of the tube; this was of course melted and returned to the solution before the next freezing point was determined. The measurements in diphenyl were carried out in a similar manner except that the freezing points were measured with a 1/10°, U. S. Bureau of Standards Specification, −10 to 100° thermometer.

Concentrations of 1 to 2 g. of solute per 100 g. of solvent were employed. The thermometer was read to 0.01° and, assuming an error of 0.02 in ΔT, the error in the molecular weight of a compound of molecular weight 200 would be 3.5 to 7%. With substances of molecular weight 600 and greater the results are only indicative of the order of magnitude.

Eastman catechol, purified by vacuum sublimation, was employed. The observed, uncorrected, melting points of different lots, after vacuum sublimation, varied from 103.99 to 104.03°. Its stability in an inert atmosphere at temperatures 5–10° above its melting point was satisfactory. When twelve freezing point determinations were made over a period of one hundred hours, the maximum

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(1) Smith and Howard, THIS JOURNAL, 57, 514 (1935).