elements (ΔH_f° and ΔF_f°) were calculated from the heat of combustion of ethanol,[14] the heat of formation of carbon dioxide[9] and water,[9] and the heat of hydrogenation of acetaldehyde,[8] together

TABLE III

THERMODYNAMIC PROPERTIES OF ACETALDEHYDE

T (°K.)	C_p	S°	$-(F^\circ - H_0^\circ)/T$	$H^\circ - H_0^\circ$	$-\Delta H_f^\circ$	$-\Delta F_f^\circ$
0	0	0	0	0	37.15	37.15
298.16	13.06	63.15	52.85	3.070	39.67	31.77
400	15.73	67.37	56.03	4.535	40.48	28.95
500	18.27	71.14	58.67	6.24	41.18	25.97
600	20.52	74.68	61.05	8.18	41.77	22.87
700	22.50	78.00	63.24	10.34	42.25	19.69
800	24.20	81.12	65.28	12.68	42.64	16.44
900	25.68	84.06	67.20	15.17	42.95	13.14
1000	26.96	86.84	69.03	17.81	43.16	9.81

(14) F. D. Rossini, J. Research, Natl. Bur. Stds., 13, 189 (1934).

with the other data in Table III. The absolute uncertainty in the heat and free energy of formation values is about 0.2 kcal./mole. The second decimal place is retained because of the higher relative accuracy of values at different temperatures.

Summary

The assignments of vibrational frequencies for acetaldehyde and acetaldehyde-d_4 are revised so as to agree with the heat capacity of gaseous acetaldehyde in addition to the observed spectra and the product rule. A potential barrier to internal rotation of 1000 cal./mole is found to give best agreement with thermodynamic data which include the equilibrium with hydrogen and ethanol in addition to the heat capacity of gaseous acetaldehyde. A tabular summary of thermodynamic properties is given.

Metal–Nicotine Double Sulfates

BY CLAUDE R. SMITH

The inorganic double sulfates represented by the formula $R_2M(SO_4)_2 \cdot 6H_2O$, where R is an alkali metal, thallium or ammonium, and M is Cu, Mg, Zn, Fe, Co, Ni, Mn or Cd constitute an important isomorphic group of compounds. Although slight variations in crystal measurements and other physical properties occur, they appear to be largely determined by some property of the univalent R-metal or radical rather than the specific M-metal.

The metal–nicotine double sulfates described here contain the bivalent cations of the M-metals and also the trivalent cations of Fe, Cr and Al. No similar group of double sulfates containing nicotine or other organic base has been reported previously. This study forms part of an extensive investigation in this Laboratory on the coördination of nicotine in forming nicotineammine and double salt compounds.

Experimental

Compounds 1 to 7, inclusive, in Table I represent the addition of "neutral" nicotine sulfate ($2C_{10}H_{14}N_2 \cdot H_2SO_4$) to the metal sulfate. The nicotine sulfate was prepared by dissolving weighed amounts of base and acid in absolute ethanol, but adjustment was made until a drop of the solution, after dilution with water, gave an intermediate tint with methyl red indicator. Number 7, however, crystallized better if nicotine was used in sufficient excess to give a yellow tint with the indicator. "Acid" nicotine sulfate ($C_{10}H_{14}N_2 \cdot H_2SO_4$), prepared by dissolving weighed amounts of base and acid in absolute ethanol, reacted directly with the normal sulfates of nos. 8, 10 and 11, but a better procedure for no. 10 was to form the sulfato-

acid $Cr_2(SO_4)_3 \cdot 3H_2SO_4$ in ethanol–water and then add the nicotine in ethanol slowly with stirring. Number 9 also was better prepared through the sulfate–acid $Fe_2(SO_4)_3 \cdot H_2SO_4$ in ethanol–water by the addition of nicotine in ethanol.

Number 1 (representative of nos. 1 to 6, inclusive) was prepared as follows: 7.5 g. (0.03 mole) of cupric sulfate was dissolved in 20 ml. of water in a 250-ml. Erlenmeyer flask, and mixed with 100 ml. of absolute ethanol containing 0.04 mole of neutral nicotine sulfate (one-third excess). Absolute ethanol was then added in 10-ml. portions until complete precipitation of the double salt occurred. After standing for several hours (or overnight), the crystals were filtered off and washed with 95% ethanol. It was dried in air but bottled as soon as dry, for it lost hydrate water under low-humidity conditions.

For no. 7, 13.4 g. (0.06 mole) of manganous sulfate tetrahydrate was used with 0.04 mole of nicotine sulfate (prepared as indicated above).

Number 8 was prepared by dissolving 0.03 mole of magnesium sulfate heptahydrate in 12 ml. of water (with gentle warming), and adding 0.04 mole of acid nicotine sulfate in 100 ml. of absolute ethanol. Absolute ethanol was then added in 10-ml. portions until a suspension of the crystals was formed. After standing, the crystals were filtered off and washed with absolute ethanol. It was dried to constant weight in a desiccator with renewed amounts (a few grams) of calcium chloride. If properly prepared, it was not appreciably hygroscopic.

Number 9 was prepared from Monsel's salt, $Fe_4(SO_4)_5 \cdot (OH)_2 \cdot 10H_2O$, following the equation $Fe_4(SO_4)_5(OH)_2 + 3H_2SO_4 + 4C_{10}H_{14}N_2 \rightarrow 2[Fe_2(SO_4)_3 \cdot 2C_{10}H_{14}N_2 \cdot H_2SO_4 \cdot 6H_2O] + xH_2O$, except that $4H_2SO_4 + 6C_{10}H_{14}N_2$ was used to provide an excess of neutral nicotine sulfate. Probably a better procedure is to dissolve 9.2 g. of Monsel's salt (mol. wt., 917.8) in a 100-ml. solution composed of 80 ml. of ethanol and 20 ml. of water containing sulfuric acid (0.04 mole) and then add 0.06 mole of nicotine in 100 ml. of ethanol. If required for a good crystal suspension, more ethanol is added.

It was dried in the same way as No. 8. It was kept in a closed container in a desiccator containing calcium chloride because it was deliquescent.

TABLE I

METAL–NICOTINE DOUBLE SULFATES

No.	Compound	Nicotine, % Found	Calcd.	SO₄, % Found	Calcd.	Metal, % Found	Calcd.	H₂O, % Difference	Calcd.	Color
1	$CuSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 8H_2O^a$	44.4	44.7	27.1	26.5	8.9	8.8	19.3	19.8	Blue
2	$CoSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 8H_2O^a$	44.4	44.9	27.6	26.6	..	..	19.5	20.0	Red
3	$FeSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 8H_2O^a$	44.5	45.1	27.6	26.7	7.9	7.6	19.7	20.1	Yellow
4	$ZnSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 8H_2O^a$	42.8	44.5	27.6	26.4	9.4	9.0	20.0	19.7	White
5	$CdSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 8H_2O^a$	41.4	41.9	25.6	24.8	..	..	..	..	White
6	$NiSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 9H_2O$	43.1	43.9	26.7	26.0	7.8	7.7	22.0	21.9	Blue
7	$2MnSO_4 \cdot 2RN_2 \cdot H_2SO_4 \cdot 11H_2O$	34.9	35.1	32.2	31.2	11.9	11.9	20.7	21.5	White
8	$MgSO_4 \cdot RN_2 \cdot H_2SO_4 \cdot 6H_2O$	32.4	33.2	40.5	39.3	5.3	5.0	21.3	22.1	White
9	$Fe_2(SO_4)_3 \cdot 2RN_2 \cdot H_2SO_4 \cdot 6H_2O$	34.6	34.9	40.8	41.3	11.2	12.0	13.2	11.6	Maroon
10	$Cr_2(SO_4)_3 \cdot 3RN_2 \cdot 3H_2SO_4 \cdot 6H_2O$	38.0	38.0	42.8ᵇ	44.9	8.4	8.1	8.2	8.4	Green
11	$Al_2(SO_4)_3 \cdot 2RN_2 \cdot 2H_2SO_4 \cdot 14H_2O$	29.0	29.1	42.9	43.1	5.6	4.9	22.1	22.6	White

ᵃ RN_2 is an abbreviation of $C_{10}H_{14}N_2$. ᵇ SO_4 contaminated the $Cr(OH)_3$ removed before estimation.

Number 10 was prepared by the following method: A 25-ml. aliquot of a chromic sulfate solution (anal., 0.728 g. chromic oxide) was mixed with 4 g. of sulfuric acid and evaporated to about 10 ml. on the steam-bath. The 10-ml. solution was diluted with 100 ml. of absolute ethanol, and to it was added, in small portions, 100 ml. of absolute ethanol containing 7 g. of nicotine, with stirring after each addition. The hard gray-green crystals formed did not adhere to the Erlenmeyer flask, and after standing overnight were filtered and dried. It was kept dry in the same manner as No. 9.

Number 11 was prepared by dissolving 13.4 g. (0.02 mole) of $Al_2(SO_4)_3 \cdot 18H_2O$ in 10 ml. of water and adding 0.06 mole each of nicotine and sulfuric acid dissolved in 150 ml. of methanol. After several days, a good suspension of crystals was formed, which was filtered, washed with absolute ethanol, and dried in the same way as No. 8. A better yield was obtained by adding an equal volume of ethanol. The final product was fairly free of hygroscopicity under low-humidity conditions but was preserved in a desiccator containing calcium chloride.

Discussion

Double salts containing Cu, Co, Fe, Zn, Cd or Ni have the same type formula, $MSO_4 \cdot 2C_{10}H_{14}N_2 \cdot H_2SO_4 \cdot xH_2O$, where x is probably 8 except with Ni, which may be 9. Uncertainty regarding x results in part from irregularities in composition best shown by the weight ratio $SO_4:C_{10}H_{14}N_2$, which should be 0.592:1. The metal content is probably too high, but errors in analysis and variations in water content render this criterion less useful. Number 4, which contains Zn, has the greatest deviation in the ratio SO_4: $C_{10}H_{14}N_2$, which is 0.641:1. On evaporation, its saturated water solution deposited two kinds of crystals. The first might have been $ZnSO_4 \cdot 7H_2O$, but later a uniform deposition of the double salt took place because nicotine sulfate was then in excess. Number 1 is probably the purest double salt of the group, with $SO_4:C_{10}H_{14}N_2$ in a ratio of 0.612:1, although its water content may vary because of humidity conditions. When dried over sulfuric acid, No. 1 lost 19.75% H_2O; there was no further loss at 110°; H_2O by difference was 19.8%. In dry weather No. 1 may lose about 6 moles of water, changing from medium blue to dark blue, but the color is not so dark as that of the anhydrous compound. After

several days' drying over sulfuric acid, all other double salts lost only about 6 moles of water. Number 3 was light yellow and quite stable in the dry state, but some oxidation occurred during preparation. The lightest colored crystals were obtained by dissolving powdered $FeSO_4 \cdot 7H_2O$ in a nicotine sulfate–water solution (containing the proper amount of water) and promptly precipitating with ethanol. A two-phase liquid was first formed, which later separated into a suspension of the double salt in the ethanol–water solution. Two-phase liquids were usually formed with all the metals except copper and cobalt.

Number 11 was the only double sulfate in which the use of methanol appeared to be advantageous. This solvent readily dissolved Nos. 1 to 8, inclusive, and appeared unsatisfactory for their preparation. It dissolved No. 11 with difficulty, but the subsequent addition of ethanol increased yields without causing deterioration of the final product.

Each metal sulfate combines with only one nicotine sulfate, either "acid" or "neutral." Crystals were obtained by evaporation of saturated aqueous solutions of the compounds. Those with Co, Ni, Zn, or bivalent Fe were similar rhombic prisms ending in sphenoids and resembling the rhombic form of $MgSO_4 \cdot 7H_2O$; those with Cd and Cu were bipyramids and triclinic prisms, respectively; those with Mn were rectangular plates mostly stacked in piles; those with Mg were a mass of woolly needles. Compounds of the trivalent metals did not crystallize properly from water.

Preparation of all compounds except No. 11 involved a nearly complete precipitation of the metal. Yields of Nos. 1 to 8, inclusive, based on the hydrated metal sulfates, were nearly quantitative. Yields of Nos. 9 and 10 were based on analyses for metal, and were used as checks for their formulas. Double salts could not be prepared with either calcium or silver sulfate.

Summary

Metal sulfates containing bivalent cations of

either Cu, Co, Fe, Zn, Cd, Ni, Mn or Mg or trivalent cations of Fe, Cr or Al were combined with either neutral or acid nicotine sulfate to produce hydrated double sulfates. Methods of preparation and properties are described.

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

Reaction Rates by Distillation. I. The Etherification of Phenylcarbinols and the Transetherification of their Ethers[1]

BY ERNEST F. PRATT AND J. DANIEL DRAPER[2]

The results of studies directed toward the determination of the relative ease of formation of the ten possible ethers from butyl alcohol, benzyl alcohol, benzhydrol and triphenylcarbinol are reported here.

These etherifications were carried out and followed by observing the rate at which the by-product water collected when a benzene solution of equivalent amounts of two of the alcohols and a small amount of p-toluenesulfonic acid was refluxed in an apparatus equipped with an automatic water separator. Several transetherifications were studied by the same general method.

Five out of the ten ethers formed smoothly.[3] The results for these together with results for the n-heptyl and n-decyl ethers of triphenylcarbinol are given in Table I. It is evident that the rate

It appears that the decreased rates obtained with butyl alcohol as compared to benzyl alcohol (expts. 4, 5, 6, and 7) are not due to any fundamental differences in reactivity of these two alcohols. To test this point an experiment like expt. 6, except that an equivalent amount of benzyl alcohol was also present, was carried out. Benzhydryl butyl ether and benzhydryl benzyl ether were obtained in yields of 43 and 41%, respectively. This result might be expected if the carbonium ion mechanism applies.[5] It appears probable that the decreased rates with butyl alcohol are due to the fact that in benzene solution butyl alcohol is more basic than benzyl alcohol so that the butyl alcohol coördinates with and thereby "deactivates" the catalyst to the greater extent.[6,7] The same effect appeared in the

TABLE I

ETHERIFICATION OF TRIPHENYLCARBINOL AND BENZHYDROL

Expt.	Reactants		Cat. concn. moles/l.	$t_{1/2}$, minutes	Yield,[a] %	30%[d]	40%	50%	60%	70%	80%	Av.
							Reaction rate constants, minutes$^{-1} \times 10^{-3}$					
1	$(C_6H_5)_3COH$	$CH_3(CH_2)_3OH$	0.0005	25.6	93	31.2	31.6	32.1	32.1	32.3	32.6	32.0
2	$(C_6H_5)_3COH$	$CH_3(CH_2)_6OH$	.0005	23.8	91	32.3	32.4	33.8	35.2	36.2	36.4	34.4
3	$(C_6H_5)_3COH$	$CH_3(CH_2)_9OH$	.0005	25.3	91	32.8	33.2	34.2	33.1	34.6	35.5	33.9
4	$(C_6H_5)_3COH$	$CH_3(CH_2)_3OH$	.00025	59.4	..[c]	11.2	11.4	11.8	12.1	12.2	12.1	11.8
5	$(C_6H_5)_3COH$	$C_6H_5CH_2OH$	.00025	18.4	90	44.1	43.5	43.8	43.3	42.5	42.3	43.2
6	$(C_6H_5)_2CHOH$	$CH_3(CH_2)_3OH$	.0020	303.0	93	2.45	2.43	2.52	2.53	2.53	2.46	2.49
7	$(C_6H_5)_2CHOH$	$C_6H_5CH_2OH$	.0020	76.1	96	10.1	10.0	10.1	10.4	10.8	11.0	10.4
8	$(C_6H_5)_2CHOH$	$(C_6H_5)_2CHOH$[b]	.0020	35.8	95	25.2	23.6	26.0	26.7	26.5	25.4	25.6

[a] Yield of once distilled or once recrystallized product. The yield of water was almost invariably 98 to 100%. [b] 0.125 mole of benzhydrol used instead of 0.125 mole of each of two alcohols as per the standard procedure. [c] Product not isolated. [d] Values in this column calculated from data taken when reaction 20 and 30% complete; values in 40% column calculated from data at 20 and 40% complete, etc.

of etherification of triphenylcarbinol is independent of the chain length of the second alcohol (expts. 1, 2 and 3); that the rate more than doubles when the catalyst concentration is doubled[4] (expts. 1 and 4); and that triphenylcarbinol is etherified much more easily than is benzhydrol (expts. 4, 6, 5 and 7).

transetherification of dibenzhydryl ether (Table II).

The absence of dibenzhydryl ether in the products of expts. 6 and 7 although this ether forms very readily (expt. 8) may, perhaps, best be ascribed to the fact that there is less steric hindrance when butyl or benzyl alcohol reacts in place of benzhydrol. The relatively high rate in expt. 8 in spite of the steric hindrance suggests

(1) From a portion of a thesis presented by J. D. D. in partial fulfillment of the requirements for the Ph.D. degree, Sept. 1947.

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(3) Related etherification studies have been made by Norris and Rigby, THIS JOURNAL, **54**, 2088 (1932), by Senderens, Compt. rend., **188**, 1073 (1929), and earlier papers, and by Ward, J. Chem. Soc., 2291 (1927).

(4) A referee has pointed out that this is inconsistent with the carbonium ion mechanism (ref. 5) unless a very large salt effect exists. This point is being further investigated.

(5) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 300.

(6) In these benzene solutions the coördination may involve formation of a hydrogen bond with a molecule of un-ionized p-toluenesulfonic acid rather than reaction with a proton.

(7) A modification of the procedure used here is being applied in an investigation of the relative basicity of alcohols, ethers and other extremely weak bases.