Nature of Calcium Acetate

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A STUDY of the hydrates of calcium acetate verified earlier work reported in the literature and showed that the anhydrous forms of calcium acetate may be obtained by heating the mono- or half-hydrate. The anhydrous forms and the half-hydrate may exist with adsorbed water at some temperatures without forming mixtures of hydrates.

In 1960, three anhydrous forms of calcium acetate had been isolated and characterized (*7*). At least one earlier report in the literature discussed the synthesis of anhydrous calcium acetate (*1*). In addition to the anhydrous acetate, both the monohydrate and half-hydrate had been established as distinct crystalline species (*2, 8*). There is also a report that the dihydrate exists, although it has not been well characterized (*5*).

In no case, however, was there any indication of the behavior of the hydrates on being heated below the decomposition point of calcium acetate or whether the anhydrous forms could be obtained from the hydrates at sufficiently high temperatures. Calcium acetate monohydrate was heated at constant temperatures, and the changes in chemical composition and crystalline structure were observed.

EXPERIMENTAL

Calcium acetate monohydrate was prepared by recrystallization of calcium acetate (analytical reagent grade, Mallinckrodt) from water-acetone. An aqueous solution of acetate was first filtered to remove carbonates, and the calcium acetate was precipitated by the addition of acetone (C.P.) to the solution. After filtration, the calcium acetate was dried in air. The x-ray diffraction pattern was identical with that reported in the literature (*8*) for the monohydrate and indicated that no mixture with other hydrated forms was present. Analysis. Calculated for $CaC_4H_8O_5$: Ca, 22.70%; C, 27.25%; H, 4.58%; H_2O, 10.24%; CO_3, 0.00%. Found. Ca, 22.47 ± 0.06%; C, 27.3 ± 0.1%; H, 4.58 ± 0.07%; H_2O, 11.5 ± 0.2%; CO_3 less than 0.01%.

The calcium acetate monohydrate was heated at constant temperatures (within 1° C.) in a constant temperature oven and in a Chevenard thermobalance, photographic type, converted to graphic recording by using a photocell circuit. Samples heated in the oven were in glass vials which were sealed with sealing wax as soon as the vials were removed from the oven; each sample was heated for 1 week. Weight losses were measured in the thermobalance with an absolute precision of ± 0.55% after no further weight change took place for one half hour. Differential thermal analyses were performed at the rate of 5° C. increase in temperature per minute, using the thermobalance furnace, a Fisher Recordall to determine the differential temperatures, and a Leeds and Northrup temperature recorder to indicate the temperatures of the sample, reference material, and furnace.

Chemical analyses were conventional: carbon and hydrogen by the combustion method; calcium by gravimetric analysis; water by the Karl Fisher method; and carbonate by liberation of carbon dioxide with acid (*4*). X-ray diffraction patterns were obtained with a Norelco diffractometer using Cu $K\alpha$ radiation, λ 1.542, and a nickel filter.

A dry distillation of calcium acetate monohydrate was performed by heating 200 grams in a round-bottomed flask equipped with a mechanical stirrer and set up for distillation into a flask cooled in a dry ice–acetone bath. The flask was heated by an oil bath kept at 200° to 240° C., and a slight vacuum was applied to the system to accelerate the distillation. After 6 hours of heating, 18.6 grams (9.3% by weight of the original material) of a colorless liquid were obtained, which analysis showed to be water (Table I). The residue from the distillation had a carbonate content of less than 0.01%.

RESULTS AND DISCUSSION

Analysis of the calcium acetate monohydrate heated in the oven at different temperatures is shown in Table II, along with the calculated analysis for each hydrated form. The crystalline forms were identified on the basis of comparison with the x-ray diffraction patterns reported in the literature (*7, 8*).

Observations of both the oven-heated material and the one from dry distillation showed that no decomposition other than dehydration had occurred up to 260° C. Between 38° and 66° C., sufficient water was lost from the monohydrate to form the half-hydrate. An interesting observation is that the x-ray patterns showed no mixture of mono- and half-hydrates, even when the sample contained more water than calculated for the half-hydrate (as little as 1% of the monohydrate in the half-hydrate is detectable in the x-ray pattern). Such a system seems to be stable even when exposed to air at room temperature. Since the monohydrate, once formed, also appears to be stable at room temperature, the behavior of the half-hydrate indicates that its conversion to monohydrate is slow.

When the loss of water exceeded that calculated for the half-hydrate, the intensities of the reflections in the x-ray diffraction patterns decreased, until an amorphous material was obtained containing about 1% water. This material has been characterized as anhydrous by Walter-Levy (*7*). Further heating produced the β-and α-anhydrous forms, each of which can be isolated in the pure state, if the temperature is held within narrow limits for a long enough time.

Because some water was associated with the anhydrous acetates, the question arose whether they were all truly anhydrous material associated with some adsorbed water or whether one of the forms might be a hydrate. It is difficult to answer this question without carrying out a

Table I. Analysis of Distillate from Calcium Acetate Monohydrate

Test	Results
Reaction with *p*-nitrophenylhydrazine solution in acetic acid–water[a]	None
Reaction to pH paper; Congo Red paper	Neutral
Qualitative solubility in ether	None
Qualitative solubility in water	Complete
Ash	None
Combustibility	None
Melting point and freezing point	0° C.
Boiling point	99–100° C.
n^{20}_D	1.3344

[a] This is specific test for ketones, indicated by formation of a precipitate (p-nitrophenylhydrazone). In this case it was used to determine whether acetone (one of the decomposition products of calcium acetate) had formed during distillation (*9*).

Table II. Analyses of Monohydrate Heated at Constant Temperatures

Temp., ° C.	Calcium, %	Water, %	Carbonate, %	Crystalline Form (X-Ray)
38	22.55±0.15	11.5±0.1	<0.01	Monohydrate
66	23.20±0.20	9.2±0.1	<0.01	Half-hydrate
93	24.00±0.20	4.7±0.1	<0.01	Half-hydrate
149	25.00±0.30	1.9±0.0	<0.01	Half-hydrate
177	25.10±0.10	1.0±0.0	<0.01	Amorphous anhydrous
221	25.20±0.30	0.52±0.00	<0.01	β-anhydrous
260	25.30±0.00	0.93±0.00	<0.01	α-anhydrous
		Calcd. Analysis		
	22.70	10.25	...	Monohydrate
	23.92	5.38	...	Half-hydrate
	25.32	0.00	...	Anhydrous

Table III. Behavior of Monohydrate in Thermobalance and on Subsequent Exposure to Air

		Calcium, %		After Exposure	
Temp., ° C.	Wt. Loss, %	Before exposure	After exposure	Water, %	Carbonate, %
100	4.74	24.47	22.61	...	<0.01
200	10.67±0.55	24.96	23.89	7.0	...
220	10.94±0.20	25.20±0.30	...	4.8	<0.01
240	11.18±0.06	...	...	2.4	<0.01
250	11.80	...	...	...	...
260	11.18±0.02	25.20±0.00	...	...	...
280	11.35±0.08	...	...	...	<0.01
300	11.41±0.28	25.38	23.89	3.0	...
350	11.61±0.20	...	...	2.4	<0.01
370	12.02	...	...	1.4	<0.01
390	11.63	...	...	...	<0.01

Table IV. X-Ray Diffusion Patterns of Calcium Acetate

Monohydrate		Half-Hydrate		β-Anhydrate		α-Anhydrate	
D-spacing, A.	Relative intensity	*D*-spacing, A.	Relative intensity	*D*-spacing, A.	Relative intensity	*D*-spacing, A.	Relative intensity
10.7	4	16.7	75	15.5	30	10.8	58
9.8	100	11.7	100	9.6	100	10.3	100
6.70	7	8.6	37	9.2	34	9.8	86
6.03	6	8.4	63	7.9	16	7.8	14
5.92	4	7.5	47	7.3	6	6.43	18
5.53	8	6.98	15	6.65	12	6.30	26
5.28	7	6.45	15	5.97	6	5.97	20
5.15	6	5.57	29	5.35	6	5.45	8
4.93	6	5.30	10	5.02	6	5.18	8
4.38	1	4.18	9	4.83	4	4.92	7
4.13	8	3.93	9	4.50	6	4.47	6
4.05	5	3.87	22	4.40	8	4.25	5
3.97	4	3.66	3	4.25	10	4.15	10
3.78	28	3.52	32	4.11	6	4.07	8
3.65	15	3.42	19	3.97	10	3.92	6
3.62	20	3.35	24	3.90	10	3.82	6
3.52	19	3.28	31	3.85	4	3.68	4
3.33	24	3.22	15	3.75	8	3.57	5
3.28	34	3.02	10	3.66	16	3.53	7
3.23	37	2.95	10	3.64	17	3.48	20
3.20	26	2.86	12	3.61	10	3.34	11
3.03	2	2.74	6	3.47	26	3.27	18
2.98	7	2.68	8	3.32	14	3.13	10
2.94	5	2.62	7	3.18	6	3.07	14
2.91	7	2.56	10	3.10	6	2.98	10
2.81	1	2.52	6	3.06	7	2.80	4
2.75	8	2.39	12	2.98	6	2.70	6
2.66	4	2.34	8	2.96	14	2.64	3
2.43	26	2.32	8	2.90	8	2.54	4
2.39	2	2.28	7	2.83	10	2.46	3
2.34	5	2.18	6	2.79	8	2.39	8
2.19	4	2.14	12	2.67	8	2.35	3
2.18	5	2.10	10	2.61	4	2.31	4
2.15	6	2.06	8	2.53	6	2.26	8
2.11	5	2.01	6	2.30	6	2.22	8
2.10	6	1.97	6	2.27	6	1.97	6
1.97	4	1.86	8	2.23	10		
1.94	5	1.76	6	2.18	6		
1.90	3			2.13	8		
1.88	3			2.11	10		
1.84	1			2.06	8		
1.81	4						
1.79	2						

vapor pressure study at high temperatures. However, a strong indication that the α-and β-forms are both anhydrous is provided by analysis of the α-acetate as it picks up moisture. Exposure to air for a few days showed a gradual increase in water content with a change in the x-ray diffraction pattern to mixtures of the α-anhydrous acetate and half-hydrate; no β-form appeared. If the β-form were a hydrate, it is likely that it would have been present. Apparently, the β-form is metastable and can be made only by heating the hydrates.

The behavior of the monohydrate in the thermobalance showed that the weight lost at temperatures above 220° C. accounts for essentially all the water present in the monohydrate. Table III illustrates this and shows what happens when the acetate samples were exposed to air at room temperature after being heated. On cooling, these samples behaved as previously reported (*7*). They picked up moisture at different rates to form the half-hydrate; the amorphous-anhydrous form reacted most quickly. In this study no decomposition was observed, even up to 390° C. The decomposition observed by Walter-Levy may have been due to longer exposure at the high temperatures.

Differential thermal analysis showed major heat absorption in the temperature ranges where other experiments showed phase changes occurring. The following tabulation summarizes these observations.

Temp. Ranges of Heat Absorption, ° C.	Phase Formed
80–150	Half-hydrate
195–215	Amorphous and β-anhydrous forms
240–275	α-anhydrous form
400–430	Decomposition to $CaCO_3$

The x-ray diffraction patterns of all the crystalline forms of calcium acetate agree with those published by Walter-Levy (*7, 8*). The pattern for the monohydrate is similar to that reported earlier by Hanawalt (*3*), but different from that shown in the ASTM x-ray powder data file (*6*). The latter pattern is similar to that observed for the half-hydrate. Hanawalt's x-ray pattern for anhydrous calcium acetate (*3*) is also different from that observed in this study. The detailed x-ray patterns with the relative numerical intensities are shown in Table IV.

Two of the hydrates and the three anhydrous forms of calcium acetate now appear to be well characterized and their behavior on heating is understood. The anhydrous forms can be obtained directly by heating the hydrates. Some further work is planned to determine whether calcium acetate dihydrate truly exists, and if so, to characterize it as well as possible and to obtain its x-ray diffraction pattern.

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Effect of Phosphorus Deposit Modifiers on Gasoline Octane Quality

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ORGANOPHOSPHORUS compounds are widely used in leaded gasoline to control surface ignition and spark plug misfiring. Of the many factors influencing the choice of a specific compound, its effect on gasoline octane quality is one of the most important. Nevertheless, except for the patent literature (*5*), there has appeared little, if any, discussion of the factors which affect the action of phosphorus compounds on octane number. This series of studies was undertaken to define the mechanism of the proknock action of phosphorus compounds and to relate such action, if possible, to the chemical structures of the phosphorus additives and the properties of the fuels in which they are used.

EXPERIMENTAL CONDITIONS

All studies of additive structure, whether inorganic or organic, were conducted using a motor gasoline composed of 91.5% light virgin naphtha and 8.5% heavy catalytic naphtha. Its octane characteristics were as follows:

	Octane Number	
	Research	Motor
Unleaded	71.0	69.5
With 3 cc. TEL/Gal.	87.0	85.0

The high lead susceptibility of this fuel magnifies any interaction of additive and TEL (tetraethyllead), and its low sensitivity allows a ready comparison of effects on motor and research octane numbers. While this fuel is not typical of the composition or quality of those in which phosphorus additives are commonly used, the trends observed in it have been confirmed in representative commercial gasolines.

Except where noted, all determinations were made with fuels containing 3 cc. TEL and 1.0 theory of phosphorus per gallon [1.0 theory of phosphorus is that amount required to convert all the TEL to $Pb_3(PO_4)_2$, assuming complete combustion of fuel and additives, and quantitative reaction of lead and phosphorus. Thus, 2 moles of a phosphate are added for each 3 moles of TEL]. Whenever possible, octane numbers were obtained using the direct match procedure, although some additives caused octane losses of such magnitude that this procedure was not applicable.

UNLEADED FUEL TESTS

None of the additives, organic or inorganic, had any significant effects on the octane quality of the unleaded test fuels. Thus all the octane losses described below are the results of some form of lead antagonism. In the case of the organophosphorus compounds, this can also be taken to mean that no appreciable quantities of peroxygenated free radical are produced from the additives, since such radicals are notoriously proknock whether TEL is present or not.