stronger one is also shown by the adjacent homologs, acetic and propionic acids.

The definite subtractive effect exerted by a weak fungistatic fatty acid on a strongly fungistatic fatty acid suggests (1) the presence of a molecular aggregate at the cellular interface similar to that of a dimer in non-polar solvents or (2) the adsorption of one acid molecule on the cellular surface blocks the adsorption of another molecule which is statistically equivalent to the acids acting in pairs.

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Note on the System Sodium Dichromate–Water

BY WINSLOW H. HARTFORD

While the solubility of this salt has been investigated,[1] the equilibrium conditions at temperatures below 0° have received no attention. The accompanying data and graph represent several types of measurements on sodium dichromate.

Experimental.—The sodium dichromate used was C. P. granular dihydrate, containing a small amount of the anhydrous salt. It analyzed: $Na_2Cr_2O_7 \cdot 2H_2O$, 100.3%; Cl, <0.005%; SO_4, 0.003%; Ca, <0.003%; Al, <0.002%; insoluble, 0.005%. The methods recommended by the *American Chemical Society* for potassium dichromate[2] were used in determining impurities, while the dichromate content was determined by electrometric titration.[3] All solutions were checked for dichromate content by electrometric titration.

Data for solutions saturated with either of the solid phases below 0° were determined by study of the freezing point in a 500-ml. container provided with agitator, using a 4-liter insulated jug containing alcohol to which solid carbon dioxide was added as needed for cooling. A calibrated low-temperature thermometer was used, and readings were taken on both rising and falling temperatures. Good thermal breaks were obtained and an accuracy of about 0.3° in temperature and 0.2% in dichromate content was obtained.

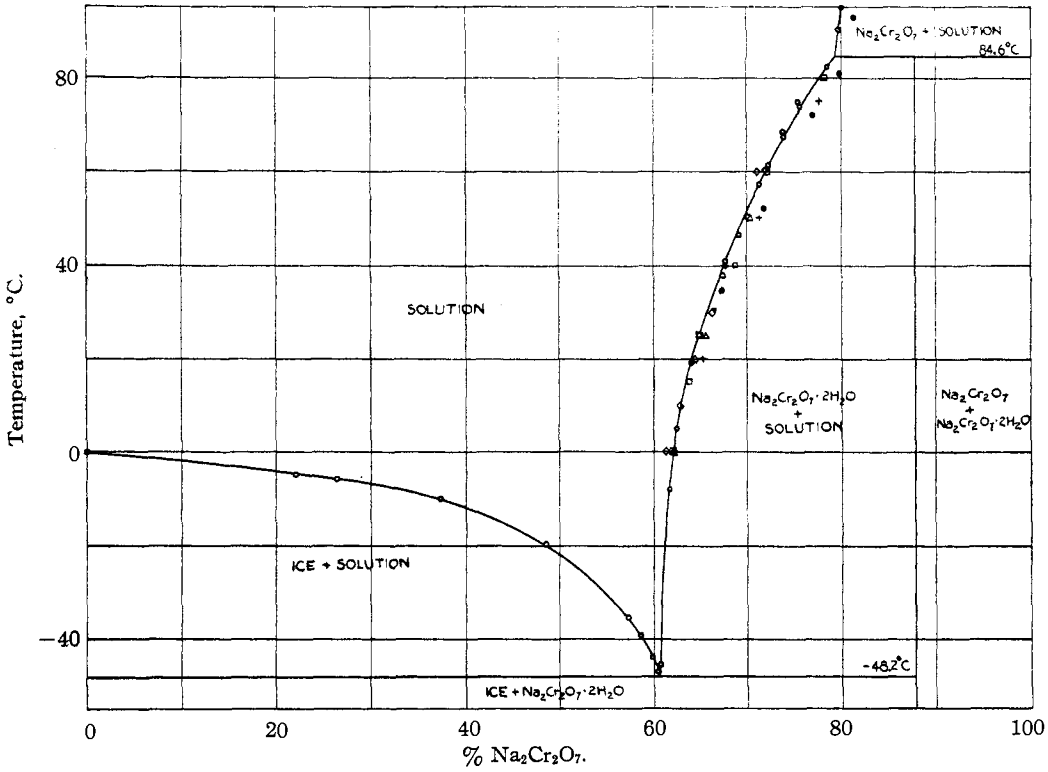

Fig. 1.—○, Hartford; ●, Mylius and Funk; ▽, Schreinemakers; +, Gerassimov; □, Rakovskii and Nikitina; △, Robertson; ◇, Yuskevich and Karzhavin.

Solubility above 0° was determined by rotating samples

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(1) (a) Mylius and Funk. *Wiss. Abhandl. physik-tech. Reichanstalt*, **3**, 443 (1900). (b) Schreinemakers, *Z. physik. Chem.*, **55**, 71 (1906). (c) Robertson, *J. Soc. Chem. Ind.*, **43**, 334 (T) (1924). (d) Yuskevich and Karzhavin, *J. Chem. Ind.* (U. S. S. R.), **3**, [14] 1119 (1926). (e) Gerassimov, *Z. anorg. allgem. Chem.*, **181**, 321 (1930); *Trans. Inst. Pure Chem. Reagents* (*Moscow*), **11**, 114 (1931). (f) Rakovskii and Nikitina, *ibid.*, **11**, 5 (1931). References published prior to 1890 have not been used in this work.

(2) Committee on Analytical Reagents, *American Chemical Society*, *Ind. Eng. Chem.*, **17**, 756 (1925); *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 171 (1929); **3**, 221 (1931); **12**, 639 (1940).

(3) Kelley and co-workers, *Ind. Eng. Chem.*, **9**, 780 (1917).

in a thermostat in the customary manner, and analysis of the clear solution obtained. The results were also checked over the range 37.6 to 74.6° by a technique involving the growth or solution of a thin crystal film.[4] In a few of these determinations, technical grade material was used, but no significant difference was noted. The accuracy of this work is of the order of 0.4° and 0.2% in dichromate content.

The transition temperature, $Na_2Cr_2O_7 \cdot 2H_2O \leftrightharpoons Na_2Cr_2O_7$, was determined by allowing a sample of about 1 kg. weight, containing a considerable quantity of suspended sodium dichromate, to cool with agitation through the transition range. The change in cooling rate was noted, and a pronounced break at the transition point measured with a calibrated thermometer with an accuracy of 0.2°.

TABLE I

EXPERIMENTAL VALUES FOR EQUILIBRIUM CONDITIONS IN THE SYSTEM SODIUM DICHROMATE–WATER

% $Na_2Cr_2O_7$ by weight	Temp., °C.	% $Na_2Cr_2O_7$ by weight	Temp., °C.
0.00	0.0	66.06	32.2
22.05	− 5.0	67.52[b]	37.6[b]
26.45	− 5.4	67.98	40.6
37.47	−10.6	69.21	46.1
48.50	−19.7	71.38	57.2
57.32	−35.7	71.76	60.0
58.90	−39.0	72.15[b]	60.9[b]
59.96	−44.0	73.82[b]	67.9[b]
60.54	−47.1	73.76	68.3
60.77[a]	E−48.2[a]	75.65	74.4
60.84	−45.4	75.43[b]	74.6[b]
61.73	− 8.0	78.41	82.2
62.17	0.0	79.18[a]	T84.6
62.49	5.0	79.65	90.1
65.01	25.0	80.01	95.0

[a] Interpolated. [b] These values obtained by film solution technique. E Eutectic. T Transition: $Na_2Cr_2O_7 \cdot 2H_2O \longrightarrow Na_2Cr_2O_7$.

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(4) This work was performed by I. Levin of this Laboratory, using an unpublished technique developed by R. B. Peet.

RESEARCH LABORATORY
MUTUAL CHEMICAL CO. OF AMERICA
BALTIMORE, MD.

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The Oxidation of Acyloins

BY BERNARD KLEIN

For several years, these laboratories have been interested in reactions conducted in glacial acetic acid.[1,2,3] The present communication is an examination of the action of ammonium nitrate in glacial acetic acid on benzoin and similar acyloins.

It was found that benzoin, in the presence of excess ammonium nitrate, at the temperature of boiling glacial acetic acid, will be oxidized to benzil in almost quantitative yield. This reaction, upon further investigation, was found to be a general one for the oxidation of acyloins. Thus, anisoin, *p*-toluoin and furoin were converted smoothly to the corresponding diketones[4]

$$RCH(OH)COR \longrightarrow RCOCOR$$
$$NH_4NO_3 \longrightarrow NH_4NO_2 \longrightarrow N_2 + H_2O$$

The above equations are substantiated by the following observations. (a) There is a copious evolution of a colorless, odorless, neutral gas, insoluble in water, immediately upon mixing the reactants. No gas is evolved when the reactants are heated independently in boiling glacial acetic acid. (b) Neither lophine[2] nor amarone[3] is produced. Hence, in the course of the reaction no ammonium acetate is formed by metathesis in any appreciable quantity. Ammonium nitrate, therefore, acts merely in the capacity of a mild oxidizing agent and can be used to oxidize sensitive α-hydroxy ketones to diketones.

Experimental

Preparation of Benzil.—To 2.12 g. (0.01 *M*) benzoin in 15 ml. of boiling glacial acetic acid, 3.2 g. (0.04 *M*) ammonium nitrate was added in one portion and the solution, once the vigorous gas evolution had subsided, was gently refluxed for one and one-half to two hours and then poured while hot into 50 ml. of cold water and placed in a refrigerator overnight. The precipitated material was collected on a filter and washed well with cold water.

Recrystallization from 80% acetic acid yielded 2.04 g. of yellow needles melting 95–96° (uncor.) A mixed melting point with an authentic sample of benzil[5] showed no depression.

No color was produced when a small amount of benzil thus made was heated with alcoholic potassium hydroxide. Benedict's qualitative reagent was not reduced.

Preparation of Anisil and *p*-Tolil.—These compounds were prepared as above (see Table I).

Preparation of Furil.—1.1 Grams of furoin, m. p. 135°, was dissolved in 10 ml. of boiling glacial acetic acid; 3.2 g. of ammonium nitrate was added in small portions as the reaction is extremely vigorous. When the evolution of gas ceased, the solution was gently refluxed for two hours. The solution was then evaporated to dryness under diminished pressure. The dry material was thoroughly extracted with butanol and the solvent evaporated to dryness under diminished pressure. The residue was crystallized from methanol (2 ml.) and then recrystallized from 80% acetic acid; yield, 0.5 g. of pale yellow needles melting at 160° (uncor.) No depression was produced when a sample was melted with an authentic sample of furil prepared by another method.[5]

Preparation of Isatin from Dioxindole.—To 0.55 g. of dioxindole[6] in 10 ml. of glacial acetic acid 3.0 g. of ammon-

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(1) D. Davidson, THIS JOURNAL, 58, 1821 (1936).

(2) D. Davidson, M. Jelling and M. Weiss, *J. Org. Chem.*, 2, 319 (1937).

(3) D. Davidson, M. Weiss and M. Jelling, *ibid.*, 2, 328 (1937).

(4) In concentrations above 0.5 *M* benzoin is converted to mixtures of benzil and unreacted benzoin—private communication, Mr. Lester Weil, Columbia University.

(5) "Organic Syntheses," Coll. Vol. I., p. 80.

(6) Marschalk, *Ber.*, 45, 583 (1912).