tween 3000 and 2100 Å. than that for the phenyl-hydrazine part of the molecule. This characteristic is exhibited, however, by several of the DNPH's prepared from apricot sirup, and suggests the possibility that it is common to a group of substances not represented in studies of known compounds. It is well known that alcoholic DNPH solutions change color from yellow to red or from yellow to blue when they are made alkaline. The resultant color has been used as the basis for colorimetric analytical methods in a number of cases. The results of work reported in this paper indicate a correlation between the color of DNPH's in alkaline ethanol solution and the degree of adsorption on magnesium sulfate. Furthermore, wide "phenyl-hydrazine adsorption" bands seem to be associated with compounds which give a blue color change in alkaline alcohol. These properties may be characteristic of a particular type of DNPH. The formation of a red color in alkaline ethanol is characteristic of simple aldehyde and ketone di-nitrophenylhydrazones, while the formation of blue colors is associated with 2,4-dinitrophenyl-hydrazine derivatives such as bis-hydrazones which form with compounds such as sugar osones, glyoxal, diacetyl and methyl glyoxal.[13] It is

(13) Neuberg and Strauss, Arch. Biochem., 11, 457 (1946); 7, 211 (1945).

not to be assumed that only bis-hydrazones give blue colors in alkaline ethanol solutions, but the fact that the blue color change is associated with bis-hydrazones and osazones is of special interest in view of the fact that apricots contain high concentrations of sugars. The possibility that sugar derivatives may be among these unknowns should not be overlooked.

Acknowledgment.—The author wishes to express his appreciation for the kind assistance and advice of Dr. G. Mackinney.

Summary

1.   A method has been described for the separation and identification of 2,4-dinitrophenylhy-drazones using spectroscopic and chromatographic methods.

2.   Furfural and hydroxymethylfurfural have been shown to be present among the intermediate compounds formed during the browning of apricots.

3.   In addition to furfurals at least 13 other carbonyl compounds are removed from apricot sirup by continuous extraction with ethyl acetate. To what extent carbonyl compounds other than the furfurals are involved in browning reactions remains to be demonstrated.

The Deterioration of Dried Fruit. IV. Spectrophotometric and Polarographic Studies

BY G. MACKINNEY AND ODETTE TEMMER

It has been shown that the so-called "browning reaction" in many dried fruits is non-enzymatic, and the effect of certain variables (oxygen, sulfur dioxide, moisture and temperature) has been reported.[1] Aqueous extracts of darkened dried apricots, like many products, frequently show a prominent absorption maximum, ca. 285 mμ. This band is due to carbonyl compounds not originally present, and sugars contribute significantly to the formation of compounds with this absorption characteristic.[2] Cantor and Peniston[3] have identified hydroxymethylfurfural in deteriorating sirups, while the mechanism of its formation from hexose and the catalytic role of amino acids has been studied by Wolfrom and Cavalieri.[4] Chromatographic procedures applied to the dinitro-phenylhydrazine derivatives[5] isolated from apricot extracts indicate a multiplicity of components, of which as yet only furfurals have been identified. It has become necessary to examine the absorption

characteristics of several aldehydes and ketones which may arise from degradation of sugar, uronic or ascorbic acids, and which may be present in the deteriorated fruit. The primary purpose of the survey has been to consider under uniform conditions, the extent to which the various compounds tested can contribute to the absorption observed, ca. 285 mμ, and the conditions under which they can be detected.

A voluminous literature exists on the absorption spectra of carbonyl compounds[6] but the data, obtained on different instruments, are scattered, various solvents were used, discrepancies are to be found, and important points may be overlooked. Thus Lewis and Calvin[7] observed that "fundamental bands of the whole conjugated system may in simpler molecules be of such low intensity as to be frequently overlooked." They added that this was the case with crotonaldehyde, in the work of Hausser, et al.[6a] This does not affect the general

(1) Ind. Eng. Chem., 38, 99, 324, 541 (1946).

(2) Paper No. I of this series, THIS JOURNAL, 70, 3576 (1948).

(3) Cantor and Peniston, ibid., 62, 2113 (1940).

(4) Wolfrom and Cavalieri, ibid., 70, 514 (1948).

(5) Paper No. III of this series, ibid., 70, 3583 (1948).

(6) E. g. (a) Hausser, Kuhn, Smakula and Hoffer, Z. physik. Chem., B29, 371 (1935); (b) Ramart-Lucas, Bull. soc. chim., 51, 289 (1932); (c) Tables Annuelles Int. de Constantes et Données Numeriques, Paris, 1930, et seq.

(7) Lewis and Calvin, Chem. Revs., 25, 273 (1939).

TABLE I

MOLAR ABSORPTION COEFFICIENTS (ϵ) IN LITERS PER MOLE CM.

	λ max (in mμ)	ϵ	λ_{min}	ϵ	λ_{max}	ϵ
Acetone	270	17.6	...	....	...	.....
Methyl ethyl ketone	277.5	17.9	225	2.6	...	.....
Acetaldehyde	277.5	8.1	...	....	...	.....
Propionaldehyde	277.5	13.1	255	8.3	210	31.8
Butyraldehyde	282.5	13.5	250	5.6	225	11.7
Dihydroxyacetone	265	17.8	230	2.3	...	.....
Methylglyoxal	282.5	27.5	225	3.5	...	.....
Glyoxal	267.5	5.8	250	5.6	...	.....
Acrolein	315	25.5	260	1.7	210	11,540[a]
Pyruvic acid	317.5	19.9	290	15.7	(210)[b]	1,302
Levulinic acid	270	25.1	240	14.3	...	.....
Crotonaldehyde	310	31.8	295	30.8	220	12,620[a]
Furan	290	1.4	270	0.8	230	4.6
Furfuryl alcohol	280	0.3	250	0.1	220	9.0
Furfural	277.5	14,800	240	1470	230	2305
Hydroxymethylfurfural[c]	282.5	16,900	245	1030	228	1900
bis-(5-Formylfurfuryl) ether	282.5	28,600	245	5250	230	6000
Furoic acid	245	11,550	215	4520	...	.....
Furoate	245	12,290	230	8570	215	31,970
Furoamide	255	12,220	225	4770	...	.....
Furil	302.5	17,260	255	4460	227.5	9350

[a] Beer's law is not obeyed in the progressive dilutions needed to record these peaks. [b] Parentheses indicate no maximum. [c] As a result of over a dozen determinations, the statement seems warranted that the band at λ_{228} rises on standing. Pure white crystals can be obtained by centrifuging the semi-molten mass at 25–28°. The value at λ_{283} shows little change, but at λ_{228} it increases from 1900 to 3750. Chromatographing the hydrazone still indicates traces of two other zones. Results may be compared with those tabulated by Singh, Dean and Cantor, THIS JOURNAL, 70, 519 (1948), Table I. By the conventional method, our material might be reported with m. p. 31° (the bath temperature for complete melting) but we consider a value of 29–30° to be more nearly correct for our product. [d] The bis-(5-formylfurfuryl) ether, recrystallized from ethanol from a sample obtained through courtesy of Dr. L. F. Wiggins, melted at 114° cor.

considerations of these classic papers, but it is of considerable importance in the present problem where such compounds as acrolein, propionaldehyde, methylglyoxal, etc., must be evaluated, with relatively low absorption in the region ca. 285 mμ.

A detailed comparison of present results with those embodied in the literature does not seem relevant here, since agreement is good in general, and where divergences are to be found, there is no reason as yet to prefer one set of values to another. Herold[8] gives a general value of 1.20 to 1.40 for the coefficients, (log k), for the lower aldehydes in hexane for the band between 260 and 300 mμ. Values in water are lower, and this is ascribed to acetal formation. Log k values for propionaldehyde are from 0.92 to 1.00 (i. e., in terms of ϵ, 8.3 to 10.0; cf. 13.1 Table I). Our aldehyde values are in general higher though the ketones show much closer agreement. However, comparisons at single wave lengths are not particularly useful. For critical comparisons, the curves as a whole must be examined. The data presented here have to be related to a natural phenomenon (the darkening) which takes place in an aqueous medium, and, as noted earlier, the primary purpose lay in determining the type of compound that could contribute to the massive increase in absorption in the region of 285 mμ.

(8) Herold, Z. physik. Chem., B18, 273 (1932); 5, 124 (1929).

Spectrophotometry

Methods.—The Beckman quartz spectrophotometer was used throughout. Slit widths varied from ca. 0.20 to 0.25 mm. at 280 mμ, to 1.8 mm. at 210 mμ. Measurements were made in the region 350 to 205 mμ. Except for furan (determined in 80% methanol), the solvent was water, and the pH was normally between 2 and 5, but in the case of furfural measurements were made at several pH values.

Determination of Concentration.—As a general check, solutions immediately prior to dilution, (where necessary) for spectrophotometric analysis were titrated with hydroxylamine to determine their carbonyl content. The sensitivity of this method can be relied on within 2% for solutions subsequently diluted 0.005 M with respect to carbonyl. Values for acetone, ca. 0.07 M, did not differ by 1%, whether based on weight or on the titration.

Pure liquids were re-distilled in vacuo, and refractive indices were checked in addition. To minimize change, pure liquids were added to weighing bottles containing 5 to 10 ml. of water, the bottles re-weighed and the contents made to volume and diluted as necessary.

The lower saturated aldehydes were prepared by chromic acid oxidation of the appropriate alcohol and estimated with hydroxylamine. Constants obtained from different preparations were reproducible within 1%.

Furfural (Quaker Oats Company) was redistilled *in vacuo;* the colorless distillate gave an $n^{22}D$ of 1.524. On exposure to air, even at 0°, furfural slowly becomes brown. Redistilled from very brown furfural, the colorless distillate gave definitely higher absorption (13% higher at 277 mμ than the value reported in Table I) and a smaller ratio of the main maximum at 277 mμ to the minimum at 245 mμ than was the case with distillates from the furfural as received. Partition with ether and retransfer to water gave a spectrum closer to that of the original. The pH had no effect, from 2.0 to 10.0 on the spectrum in the range 320 to 230 mμ, but below 230 mμ a second minimum, *ca.* 210 mμ, was observed on the alkaline side.

Hydroxymethylfurfural was prepared by the method of Haworth and Jones.[9] When distilled, a colorless distillate was obtained, which while still under high vacuum became yellow. The crystals obtained overnight at 0° were also yellow. Determined immediately, the absorption constants agreed with those of the distillate, run immediately, but on prolonged standing, they gave progressively lower values, and required redistillation. The influence of pH was in the region below 230 mμ, with a second minimum as in the case of furfural, noted above.

Acrolein (courtesy of Shell Development Company) $n^{20.3}D$ 1.4012, was determined twice, and the values for the absorption coefficients checked within 1%.

Dihydroxyacetone was prepared from glycerol with *Acetobacter suboxydans* (courtesy of Dr. H. J. Phaff) and was the dimer, since it melted at 82°.[10] As with glyoxal (Carbon–Carbide) and methylglyoxal, one is almost certainly examining an equilibrium mixture. A similar mixture would no doubt exist in the natural concentrates if these components are present.

Methylglyoxal was prepared from dihydroxyacetone by distillation from 20% sulfuric acid. Concentrations were determined by oxidation with hypoiodite, assuming eight equivalents of iodine per mole[11] and 94% completion of the reaction.[12] Five different preparations were made, the concentrations varying from 0.2 to 0.95 g. per liter. The iodine values checked within 7% those estimated with hydroxylamine. From the ten analytical values so obtained on the five preparations, ten values of the molar absorption coefficient ϵ can be calculated, and we believe the values reported in Table I are correct within ±2 units. Greater accuracy is not warranted because the spectrum changes within one hour, a marked lowering of the minimum being observed. The iodine and hydroxylamine values however, are not changed, nor is the ability of the solution altered in the yielding of iodoform or an osazone, m. p. 150°, soluble in acetone.

(9) Haworth and Jones, *J. Chem. Soc.*, 667 (1944).
(10) Strain, THIS JOURNAL, **56**, 2649 (1934).
(11) Fischler and Boettner. *Z. anal. Chem.*, **74**, 32 (1938).
(12) Woo and Chang, *J. Chem. Soc.*, 162 (1945).

Except for furan (courtesy of E. I. du Pont de Nemours & Co.) and acetone C. P., the remaining compounds were from Eastman Kodak Company, and were not further purified.

Results are shown in Table I.

Discussion

On examination of a sequence in Table I for acetone, dihydroxyacetone, methylglyoxal, propionaldehyde, acrolein and furfural, the values for ϵ at the maximum for the longer wave length are 17.6, 17.8, 27.5, 13.1, 25.5 and 14800, respectively.

A second peak above 200 mμ is found for propionaldehyde 31.8; acrolein 11500, furfural 3500. The effect of the double bond at the longer wave length for acrolein is thus 25.5, compared with 13.1 for its saturated analog, propionaldehyde. Furan itself has negligible absorption so that the characteristic furfural spectrum must be due to an effective resonance not possible in the other cases, an oxonium on the oxygen in the ring apparently as effective a resonator as, *e. g.*, p-hydroxybenzaldehyde,[13] log ϵ 4.24 at 284 mμ.

It may readily be computed that equal optical densities will be obtained at the respective peaks with furfurals, *ca.* 0.003, acetone 1.9 and furan 23 g. per liter, respectively, and it is clear that structures such as furfurals will mask the presence of other aldehydes and ketones that may be present. It is interesting that glyoxal itself has the lowest value of any under consideration, and it is difficult to postulate an effective resonance, *i. e.*, to formulate an effective charge separation for this compound as can be done with furfural, for example. The similarity of acetone and dihydroxyacetone, including the expected shift owing to hydroxy substitution, makes it unlikely that the monomer, dissolved in water, would have yielded a result different from that obtained with the dimer.

Polarography

The foregoing section makes it evident that spectrophotometric measurements are particularly useful in determining the furfurals, even in low concentration, but of little value in detecting such compounds as methylglyoxal, particularly in the presence of furfural. The polarographic method was therefore considered as a possible approach in which it was hoped that furfurals would not mask the presence of other carbonyl compounds. Three aspects are considered here:

1. The half wave potentials of several pure compounds.

2. The waves to be observed in buffered aqueous extracts of both darkened and undarkened apricot extracts. (This includes examination of extracts partitioned with ether or ethyl acetate.)

3. The relation between furfural concentration and diffusion current, and the same relation in apricot extracts.

In the last mentioned case, the furfural is computed from spectrophotometric data. Two possi-

(13) Morton and Stubbs. *J. Chem. Soc.*, 1347 (1940).

bilities exist: (a) that the wave is due solely to furfural (the plot of diffusion current vs. concentration will coincide with the plot for pure furfural) and (b) that the wave is due in part to other compounds (a greater diffusion current will be observed for a given apparent furfural concentration). The latter was in fact observed (Fig. 1) and the conclusion may be drawn that the wave is due in large measure to non-furfural components which are not masked here, though the waves are not as yet separable from that of the furfurals.

Methods.—The Fisher Elecdropode was used, and the characteristics of the capillary included a drop time of 4.933 sec. and 1.872 mg. of mercury dropping per sec. The supporting electrolyte was in all cases 0.1 N potassium chloride. Phosphate buffers were used for pH 7.0, biphthalate, ca. pH 4.0, and hydrochloric acid was added for low pH values. The suppressors were bromcresol green and methyl red, 0.0005%.

Fig. 1.—Diffusion current vs. furfural concentration: O, furfural, pH 4.0; △, furfural with undarkened sirup, pH 4.0; □, darkened apricot sirup, aqueous extract, pH 4.0; ●, darkened apricot sirup, ethyl acetate extract, pH 4.0.

TABLE II

HALF WAVE POTENTIALS vs. S. C. E., IN VOLTS

	pH	$E_{1/2}$
Pyruvic acid, cf. Ref. 14	3.1	−0.99
Dihydroxyacetone	4.5	−1.60
Glyoxal, cf. Ref. 15	3.4	−1.41
Methylglyoxal	4.5	−0.83
	7.1	−1.04
Acrolein	4.5	−1.36
Furfural, cf. Ref. 16	2.8	−0.99
	3.9	−1.06
	7.1	−1.32
	7.6	−1.38
Hydroxymethyl furfural, cf. Ref. 3	7.1	−1.26
Aqueous extracts		
1. Darkened apricots	2.5	−1.06
	7.4	−1.34
2 Undarkened apricots	4.0	−1.53
3 Undarkened apricots + furfural	4.0	−1.06
Ethyl acetate extracts		
1 Darkened apricots	3.9[a]	−1.32
	7.4	−1.26
		(−1.45)
2 Undarkened apricots	4.0[a]	−1.50
	7.4	(ca. −1.50)

[a] The apricot buffer system was utilized here.

The half wave potentials vs. the saturated calomel electrode are shown in Table II and are in general agreement with results in the literature. The waves for an aqueous extract of darkened apricots are not separable at pH 4 from those of furfural and certain other compounds, e. g., glyoxal, acrolein. It became of interest therefore to compute the furfural concentrations in the apricot extracts polarographically for comparison with spectroscopic values. The maximum furfural concentrations cannot exceed the value ob-
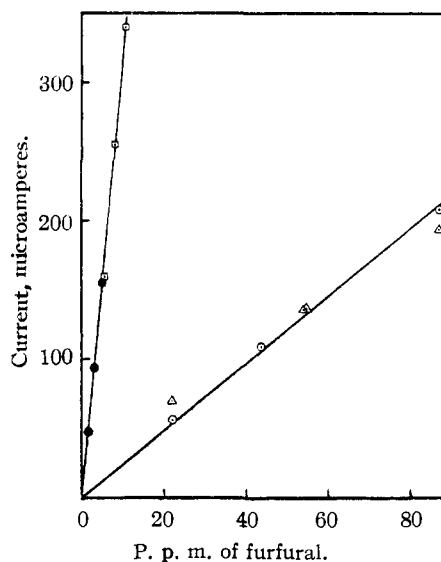
(14) Muller and Baumberger, THIS JOURNAL, **61**, 590 (1939).
(15) Winkel and Proske, *Ber.*, **69**, 1917 (1936).
(16) Tachi. *Bull. Agr. Chem. Soc. Japan*, **41**, 1371 (1938).

tained by ascribing the whole of the absorption at 280 mμ to furfurals. For convenience this is called the uncorrected value. A "corrected value" is obtained by deducting the absorption due to the non-ether extractable residue at this wave length (cf. Paper I, Fig. 3 of this series). The relation between diffusion current and concentration of pure furfural is shown in Fig. 1, together with plots for apricot extracts, calculated in terms of uncorrected (total possible) furfural, and "corrected," as mentioned above. In this set of experiments, the darkened apricot extracts had optical densities at 285 mμ equivalent to 14, 21 and 28 p. p. m. ("corrected" 5, 7.5 and 10 p. p. m., respectively), but on the basis of the diffusion currents, these are equivalent to 35, 56 and 76 p. p. m. for pure furfural. The aqueous and ethyl acetate extracts of undarkened apricots at pH 4.0 also show a wave, which, however, cannot be due to furfural, its half wave potential being ca. −1.5 v., so that the waves reported for the darkened extracts clearly developed concurrently with darkening. The absorption band at 285 mμ was absent in the undarkened extract, so that furfural itself could not have been present. In addition, in one experiment, several aliquots of furfural were added to the undarkened extract (the triangles of Fig. 1), and the furfural wave was easily detected, and its height was accounted for entirely by the quantity of furfural added.

Summary and Conclusions

Two main points which this series of papers has established are first that furfurals are present in deteriorated darkened apricots and act as intermediates in darkening and, secondly, that other

carbonyl compounds are formed, as yet unidentified, some of which may also be expected to play a role as intermediates. The present paper supports these views, the spectroscopic evidence showing the overwhelming effect of furfurals on the absorption, while the polarographic data show that the wave found in darkened extracts cannot be accounted for exclusively in terms of furfurals, as determined spectroscopically.

Thermal Transformations of Methylchlorosilanes

BY ROBERT O. SAUER AND E. M. HADSELL

The methylchlorosilanes, $(CH_3)_nSiCl_{4-n}$, apparently possess reasonable thermal stability since their synthesis has been reported at temperatures of 300 to 400°.[1] Objectives of the present study were a more precise definition of the thermal stability of these compounds and at least a qualitative knowledge of their decomposition products. In particular we sought to effect an interchange of chlorine atoms and methyl groups and to ascertain the conditions necessary to produce such interchange.

The first observation on the migration of hydrocarbon radicals attached to silicon is that of Ladenburg,[2] who reported small amounts of diethyldiphenylsilane and tetraethylsilane by the interaction of zinc ethyl and phenyltrichlorosilane at 175°. Dolgov and Volnov[3] reported a study of similar rearrangements on heating tetrasubstituted alkyl- and alkyl-arylsilanes at 300° for twenty-four to forty-eight hours with an initial pressure of 100 atmospheres of hydrogen. In addition to rearrangements these investigators noted the hydrogenolysis of silicon–carbon bonds which, in this case, resulted in the formation of disilanes and hydrocarbons. The interchange of alkyl groups in tetra-alkylsilanes was studied again by Calingaert, Soroos and Hnizda[4] who reported that a "random equilibrium mixture" containing all five possible tetraalkylsilanes was obtained by heating under reflux approximately equimolar amounts of tetraethylsilane and tetra-n-propylsilane at 175–180° for five hours with 2.5 mole per cent. of aluminum chloride.

During the progress of this work the random rearrangement of the chlorobromosilanes and the chloroiodosilanes at 600° and without a catalyst was reported.[5] With aluminum chloride "partial" rearrangement could be effected in seven hours at 140°. Interchange of hydrogen and chlorine was similarly carried out by Stock and Somieski[6] in their synthesis of chlorosilane from silane and dichlorosilane.

At the start we planned to study the thermally induced transformations of the methylchlorosilanes by heating the individual compounds up to 450° in a closed steel vessel and in the presence of a variety of inorganic chlorides as possible decomposition or rearrangement catalysts. As it soon became apparent that interchange of the substituents on silicon could be brought about, a second projection of the problem was to establish whether or not an equilibrium existed and, if so, to ascertain the concentrations of the various components at equilibrium. The nature of the side reactions, pronounced at temperatures of 375° and higher, as well as the extension of the rearrangement studies to systems containing two types of hydrocarbon radicals, logically constituted part of the broad problem.

Experimental

A. Redistribution of the Methylchlorosilanes

Reaction Conditions.—A steel Aminco rocking autoclave operated under autogenous pressure was used in our experiments. The temperature range covered was from 250°, at which temperature the extent of reaction was very small, to 450° which was about the upper limit of our heating jacket. Since the critical temperatures of the methylchlorosilanes are in the range 225–275° no liquid phase was expected during the experiments. In general about one liter of liquid methylchlorosilanes was charged to the 3.4-l. autoclave; this corresponds to about 2.3 moles per liter (gas phase). The pressures developed in the bomb were linear with temperature. In Fig. 1 some of the experimental points obtained on six 1.0-kg. charges of dimethyldichlorosilane are plotted (Curve I) to show the lower pressures obtained experimentally as compared to those predicted by the ideal gas laws (Curve II). At comparable molar concentrations substantially the same pressure–temperature behavior was shown by trimethylchlorosilane, by methyltrichlorosilane, by equimolar mixtures of these two, and by a 2:1 mixture of the former with silicon tetrachloride.

Since it was established fairly early in the investigation that aluminum chloride was an effective catalyst (whereas zinc chloride, ferric chloride, cuprous chloride and boron chloride were much inferior) in accelerating the attainment of the equilibria all of the experiments described in this paper employed either this compound or no added catalyst.

The heating times given represent the elapsed time at the stated temperature. Actually at the higher temperatures the reaction times are appreciably longer (possibly two or three hours longer) than the times given because of the heat capacity of the bomb and heater. In some cases (and these are designated as "quenched") the autoclave was removed immediately from the heater and chilled rapidly so

(1) Rochow, THIS JOURNAL, 67, 963 (1945).

(2) Ladenburg, Ber., 7, 387 (1847).

(3) Dolgov and Volnov, J. Gen. Chem. (U. S. S. R.), 1, 91 (1931).

(4) Calingaert, Soroos and Hnizda. THIS JOURNAL, 62, 1107 (1940).

(5) Forbes and Anderson, THIS JOURNAL, 66, 931 (1944).

(6) Stock and Somieski, Ber., 52, 719 (1919).