Summary

1. Crystalline dioxanates of some Group VB trihalides have been prepared and characterized.
2. Dissociation pressures of these dioxanates at 20° have been measured and the dissociation pressure of $SbCl_3 \cdot 2C_4H_8O_2$ was measured from 0 to 20°.
3. Complete dissociation of the arsenic trichloride complex in the vapor state and of all the dioxanates in benzene solution occurs.

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[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aldol Condensation. I. Detection of Carbonyl Groups in Aldols by Use of Raman Spectra

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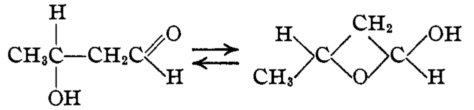
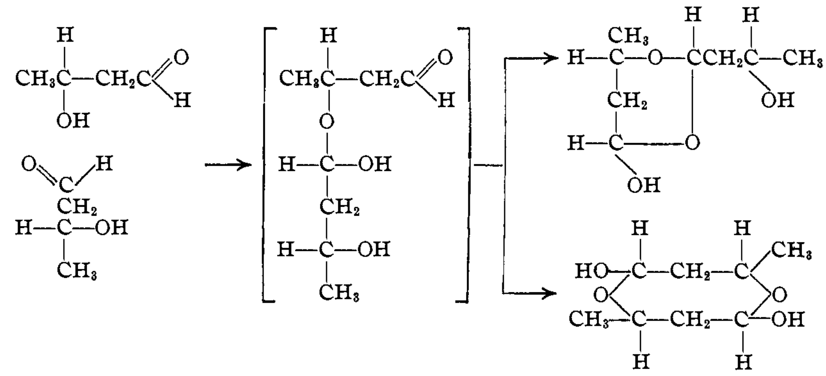
The aldols are a group of relatively unstable compounds whose structures are designated classically by β-hydroxyaldehyde formulas. The chemical reactions and physical properties of these substances indicate that such a formulation may not be entirely correct; and almost since their discovery by Wurtz[1] in 1872, investigations have been carried on which have left the structures of the aldols and their polymerization products still unsettled.[2-7]

Acetaldol has been studied most extensively, probably because it was the aldol most easily obtained. Also, it may be considered as one of the elementary sugars and from this standpoint its structure is of theoretical interest. Hurd and Abernethy[5] believe that acetaldol exists in the open chain aldehyde form in agreement with classical structures since the methylation products were all straight chain compounds. In the opinion of others,[2,4] this compound is more correctly represented by a monomeric inner hemiacetal which is in equilibrium with a small amount of the true aldehyde form. Apparently no stable derivatives of this cyclic form have been prepared. The two forms of the acetaldol in equilibrium are shown in the equation



As acetaldol ages it becomes progressively more and more viscous and finally solidifies. The solid is known as paraldol and, according to an earlier idea, its formation is due to physical interactions and involves no new chemical bonds.[8] Later researches indicate the formation of six-[6] or eight-membered,[3,7] ring compounds from two molecules of the classical aldol. This dimerization is shown below.



Spectrographic investigations of acetaldol occasionally have been reported. Backés,[4] using ultraviolet absorption spectra, found no trace of a carbonyl group in anhydrous acetaldol, but in aqueous solutions a carbonyl maximum could be observed which was intensified in the presence of hydrochloric acid. Using infrared absorption with a benzene solution of acetaldol he reported that a band at 10,000 cm.$^{-1}$, generally ascribed to tertiary OH, disappeared on standing. Hilbert,

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(1) Wurtz, *Compt. rend.*, **74**, 1361 (1872).

(2) Bergmann and Kann, *Ann.*, **438**, 278 (1924).

(3) Bergmann, Miekeley and von Lippmann, *Ber.*, **62B**, 1467 (1929).

(4) Backès, *Compt. rend.*, **200**, 1669 (1935); **207**, 74 (1938).

(5) Hurd and Abernethy, THIS JOURNAL, **63**, 1966 (1941).

(6) Späth and Schmid, *Ber.*, **74B**, 859 (1941).

(7) Hori, *J. Agr. Chem. Soc. Japan*, **17**, 1 (1941).

(8) Kohn, *Sitzber. Akad. Wiss., Wien*, IIb, **108**, 744 (1899).

Wulf, Hendricks and Liddel,[9] examining the 7000 cm.$^{-1}$ region of the infrared in a search for chelated hydroxyl groups, found that there was no evidence of chelation in acetaldol for which they apparently assumed the classical monomeric structure.

The Raman spectrum of acetaldol has been obtained prior to the present investigation, by Hibben[10] and by Backés.[4] In 1932 Hibben reported the spectrum as shown in Table I. The line at 1687 cm.$^{-1}$ he attributed to the carbonyl in the classical formula of the aldol, and the one at 1638 cm.$^{-1}$ led him to the conclusion that a tautomeric "ketol" form was present. There is scant experimental detail in his communication, especially concerning the source of his material, but certainly such a spectrum could not be obtained from pure aldol. The 1638 cm.$^{-1}$ line is no doubt due to the vibration of a carbon–carbon double bond, but the 1687 cm.$^{-1}$ carbonyl vibration must be from a conjugated aldehyde. The carbonyl frequency of unconjugated aldehydes is found near 1720 cm.$^{-1}$. The frequencies of the two lines found by Hibben are the same as those occurring in crotonaldehyde, and, although Hibben felt that crotonaldehyde was not an impurity, a comparison of the spectra in Table I shows many similarities. We have found two lines in the same positions in the spectrum of the distillate of a commercial aldol sample. However, the intensities of these two lines were reversed from what was found in the crotonaldehyde spectrum, indicating the presence of some other unsaturated aldehyde. Hibben did not report intensities so that neither an estimate of the amount of conjugated aldehyde in his sample could be made nor could the impurity be identified as crotonaldehyde.

Backés,[4] from freezing point measurements, concluded that acetaldol changed completely from the monomer to the dimer within ten minutes after distillation. With this in mind he set up a device to obtain the Raman spectrum of the sample using continuous distillation to assure himself that the monomer was present. He was convinced that his arrangement did produce the monomer, but in spite of all his precautions he obtained no carbonyl frequency near 1720 cm.$^{-1}$. He did, however, find a strong frequency at 1206 cm.$^{-1}$ which, he argued, must be due to pseudocarbonyl which he called "carbonyle XII."

TABLE I

RAMAN SPECTRA OF ACETALDOL, PROPIONALDOL, *n*-BUTYRALDOL AND CROTONALDEHYDE

Acetaldol Present $\Delta\nu$ 1	Acetaldol Backés $\Delta\nu$ I	Acetaldol Hibben $\Delta\nu$ 1	Crotonaldehyde $\Delta\nu$ 1	Propionaldol $\Delta\nu$ I	*n*-Butyraldol $\Delta\nu$ I
	248				
265 (1)		288			
			300 (3)		
					312 (4)
				334 (2)	
				365 (4)	
423 (1)				427 (2)	
453 (1)		469	464 (7)	460 (3)	
493 (6)	474 (f)			484 (5)	
538 (4)	525	545	547 (5)		
	560				
665 (1)					
	695				
				739 (1)	727 (0)
762 (3)			779 (2)	769 (1)	776 (1)
818 (4)	804 (f)	798		825 (4)	
842 (1)	838 (f)				844 (0)
871 (1)				882 (1)	898 (4)
	942 (f)			930 (1)	
970 (1b)		958		953 (5)	974 (2)
					1024 (2)
			1046 (3)	1036 (3b)	1046 (2)
1096 (2b)	1085		1084 (1)	1079 (2b)	
				1115 (2b)	1109 (2b)
					1140 (4b)
1150 (4)	1150 (F)	1156	1150 (8)	1153 (5)	
1184 (2)				1178 (2)	
	1206 (F)				
1232 (1/2)					1232 (2)
1258 (1/2)					
	1282 (f)			1277 (3b)	
		1307	1306 (7)	1312 (3b)	1300 (3)
1340 (3)	1342				1343 (0)
1377 (3)	1380 (f)		1377 (5)	1368 (3b)	
		1395	1393 (7)		1394 (1)
1452 (6)	1445 (aF)	1450	1443 (6)	1442 (8)	1452 (9)
				1463 (8)	
		1638	1642 (8)		
		1687	1688 (10b)		
					1718 (7)
2731 (1)			2736 (3)	2734 (2)	2739 (2b)
			2813 (2)		
			2844 (2)		
2876 (6)	2890 (aF)		2876 (2)	2877 (9)	2871 (10)
			2916 (8)		2908 (7)
2937 (10)		2925	2944 (3)	2941 (10)	2935 (8)
2987 (6b)		2978	2976 (3)	2976 (5b)	2969 (5)
			3004 (3)		
			3030 (3)		

The results which were obtained in the present investigation (see Table I) gave no line whatsoever at 1206 cm.$^{-1}$. The agreement of the other frequencies is only fair; however, the spectrum obtained by Backés is obviously incomplete since he reports only one line in the 3000 cm.$^{-1}$ C–H region. Since the 1206 cm.$^{-1}$ line to which so much significance is attached does not appear on our spectrograms, and since it is close to the frequency which the strong Raman line 2983 cm.$^{-1}$ would have if excited by Hg 4047 Å., it is believed that this 1206 cm.$^{-1}$ is an incorrect assignment and that therefore the postulation of this special, active carbonyl is without grounds.

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(9) Hilbert, Wulf, Hendricks and Liddel, THIS JOURNAL, **58**, 548 (1936).

(10) Hibben, *Proc. National Acad. Sci.*, **18**, 532 (1932).

In the spectrum that we have obtained for freshly prepared and freshly distilled acetaldol there is no indication of either carbonyl or ethylenic unsaturation. Any formula for the aldol condensation product, then, which contains such structural units must either be incorrect or must be so transient that its existence is only a matter of minutes. We have examined the spectrum of acetaldol several weeks after distillation and found it to be identical with that of a freshly distilled sample, in agreement with the findings of Backès. While this does not explain what happens when aldol ages, it is certain that the gradual increase in viscosity from a fairly mobile liquid, when freshly distilled, to a thick sirup after several weeks is not due to the disappearance of a carbonyl function.

The Raman spectra of propionaldol and *n*-butyraldol are given here for the first time in Table I. The spectrum of propionaldol presents the same problems as that of acetaldol. The carbonyl group, if indeed this material ever possessed one, had disappeared by the time the spectrum could be obtained, and the spectrum of the same sample a whole year afterward was still unchanged even though the material had become very viscous.

As can be seen in Table I the spectrum of butyraldol is the first of the series to exhibit a carbonyl frequency. This carbonyl has, however, only a temporary existence and can be seen to disappear gradually by observing the spectrum at various times after distillation. In Table II the intensity, obtained by microdensitometer readings, of the C–H deformation line at 1452 cm.$^{-1}$ is compared to the intensity of the 1718 cm.$^{-1}$ carbonyl line for three different exposures. At the end of two weeks the spectrum showed no trace of a carbonyl line. There were no other marked changes in the spectrum.

TABLE II

RELATIVE INTENSITIES OF THE 1452 CM.$^{-1}$ AND 1718 CM.$^{-1}$ LINES IN THE SPECTRUM OF *n*-BUTYRALDOL AT VARIOUS TIMES AFTER DISTILLATION

Sample	Relative intensities 1452 cm.$^{-1}$	 1718 cm.$^{-1}$
Immediately after distn.	10	6
Two days after distn.	10	1
Two weeks after distn.	10	Not visible

Experimental

Preparation of the Aldols.[11]—Equal volumes (about 100 ml.) of ether and freshly distilled aldehyde were mixed and cooled to 0–5° and two drops of dibutylamine added. Ten per cent. potassium hydroxide solution was then added with vigorous stirring. The temperature was regulated between 5 and 10° by cooling and by the rate of adding potassium hydroxide. When the temperature no longer tended to rise the reaction was assumed to be complete. The two layers were separated and the ether layer neutralized with 5% sulfuric acid, washed and dried with anhydrous sodium sulfate. The ether was separated by distillation and the aldol distilled under reduced pressure.

The aldols studied could not be distilled in a fractionating column without partial dehydration. Dehydration was detected spectroscopically by examining the spectrograms for the pair of lines at 1640 and 1690 cm.$^{-1}$ which are characteristic of α-unsaturated aldehydes. If these two lines could not be detected on long exposure the sample was assumed to be free of compounds formed by dehydration. The undehydrated samples were obtained by taking the reaction product and warming it to about 35° under a few mm. pressure for about an hour to drive off the ether and unreacted aldehyde. The aldol was then placed in a Raman distilling apparatus and distilled over into the Raman tube as rapidly as possible at a few mm. pressure. Only freshly prepared acetaldol samples could be distilled in this way. Samples of commercial acetaldol or acetaldol which had been permitted to age for several weeks gave little but resins and distillates containing unsaturated compounds.

The apparatus and experimental technique for obtaining the Raman spectra are described elsewhere.[12] Hg 4358 Å. was used for excitation. Exposures were about nine hours with a slit width of 0.08 mm.

Summary

1. It has been shown by means of Raman spectra that no aldehyde group is present for freshly distilled, freshly prepared samples of acetaldol and propionaldol. In the spectrum of freshly distilled butyraldol a strong aldehyde line was observed, but after the sample had aged for two weeks no aldehyde line was visible in its spectrum.

2. The change of acetaldol and propionaldol from fairly mobile liquids when first distilled to thick sirups after several weeks is not due to a gradual disappearance of a carbonyl function.

3. The Raman spectrum of acetaldol has been obtained and compared with spectra obtained previously by others. The Raman spectra of propionaldol and butyraldol have been recorded for the first time.

CHICAGO, ILLINOIS RECEIVED APRIL 9, 1943

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[11] Batalin and Slavina, *J. Gen. Chem.* (U. S. S. R.), **7**, 202 (1937).

[12] Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland and Murray, *ibid.*, **7**, 396 (1939).