ester (VI) in 20 cc. of dry ether and 4 drops of pyridine was added 15 cc. of thionyl chloride. After standing at room temperature for one hour, the ether and excess thionyl chloride were removed under reduced pressure. The acid chloride was dissolved in 50 cc. of dry ether and added to a solution of magnesio malonic ester in 100 cc. of ether prepared from 30 cc. of malonic ester and 4.7 g. of magnesium.[10] After refluxing overnight, the mixture was treated with dilute hydrochloric acid, the ethereal layer was washed with dilute sodium carbonate solution, the ether was evaporated, and the residue was distilled under reduced pressure; b. p. 170–172° at 0.4 mm.; yield, 21.1 g. (80%). The substituted malonic ester was obtained as a colorless liquid which gave a reddish-brown color with alcoholic ferric chloride.

Anal. Calcd. for $C_{16}H_{24}O_7$: C, 58.5; H, 7.3. Found: C, 58.2; H, 7.0.

cis-γ-1-**Methyl-2-carboxycyclopentyl-γ-ketobutyric Dilactone (IX)**.—To a solution of sodium ethoxide prepared from 1.33 g. of sodium and 30 cc. of absolute alcohol was added 19 g. of the above malonic ester. After the mixture had stood at room temperature for ten minutes, 10 cc. of methyl bromoacetate was added. The mixture was allowed to stand at room temperature overnight and then was refluxed for one hour. Dilute hydrochloric acid was added to the cooled mixture and the precipitated oil was taken up in benzene. The benzene solution was washed with water and the benzene was evaporated. The residue was refluxed for forty-eight hours with a mixture of 50 cc. of acetic acid and 100 cc. of concentrated hydrochloric acid. The hydrochloric and acetic acids were removed under reduced pressure and the residue was taken up in benzene. The benzene was washed with 10% sodium carbonate solution and then with water. The residue obtained by evaporation of the benzene was crystallized from benzene–petroleum ether; m. p. 152–153.5°; yield, 5.5 g. (45%). After several recrystallizations from benzene–petroleum ether the dilactone was obtained as colorless needles; m. p. 155–156°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.7; H, 6.7. Found: C, 62.9; H, 6.9.

The *cis*-γ-**1-methyl-2-carboxycyclopentyl-γ-ketobutyric acid (VIII)** was obtained by heating 3 g. of the dilactone in 4 cc. of 45% potassium hydroxide solution and 10 cc. of water until a clear solution was obtained. The solution was cooled in ice water and was acidified with dilute hydrochloric acid. The acidified solution was extracted with ether. The residue obtained by evaporation of the ethereal extract was crystallized from benzene–petroleum ether; m. p. 113.5–114.5°; yield, 2.2 g. (73%). The oily residue from the mother liquor can be reworked in the same manner and a further quantity of the free acid can be obtained. After several recrystallizations from benzene–petroleum ether the acid was obtained as colorless prisms; m. p. 114.5–115°.

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.9; H, 7.0. Found: C, 58.3; H, 7.2.

Methyl *cis*-γ-**1-Methyl-2-carbomethoxycyclopentyl-γ-ketobutyrate.**—A mixture of 2 g. of the dilactone and 40 cc. of 2.5% methanolic hydrochloric acid was refluxed for twenty-four hours. The methanol was removed under reduced pressure, benzene was added, and the benzene solution, after being washed with dilute sodium carbonate solution, was evaporated and the residue was distilled, giving the methyl ester as a colorless liquid; b. p. 172–174° at 0.6 mm.; yield, 2.13 g. (87%).

Anal. Calcd. for $C_{13}H_{20}O_5$: C, 60.0; H, 7.8. Found: C, 60.6; H, 78.

Summary

Some intermediates in a proposed synthesis of 4-keto-7a-methylhexahydroindane are described.

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[10] Lund, *Ber.*, **67**, 935 (1934).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

Raman Spectra of Aldehyde and Ketone Bisulfites

BY C. N. CAUGHLAN AND H. V. TARTAR

The structure of aldehyde and ketone bisulfites has, until recent years, been an open question. Since only one investigator has used a physical method for determining the constitution of these addition products,[1] it was deemed a worthy undertaking to determine, if possible, the type of valence bonds by means of the Raman effect.

The aldehyde and ketone bisulfites have been considered to be salts of either, (1) hydroxysulfonic acids, or (2) esters of sulfurous acid. The first structure was assigned in the beginning. Later this was abandoned because of Müller's[2] reported preparation of potassium hydroxymethanesulfonate by sulfonating methyl alcohol, which showed entirely different properties from the corresponding formaldehyde bisulfite.[3] Raschig and Prahl[4] found that the product obtained by Müller was actually dipotassium *sym*-acetonedisulfonate, formed from acetone as an impurity in the methyl alcohol used. In addition they showed that sulfonation of methyl alcohol produces methyl hydrogen sulfate, an isomer of hydroxy-

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[1] Stelling, *Cellulosechem.*, **9**, 100–102 (1928).

[2] Müller, *Ber.*, **6**, 1031 (1873).

[3] Reinking, Dehnel and Labhardt, *ibid.*, **38**, 1069 (1905).

[4] Raschig and Prahl, *ibid.*, **59**, 2025–2028 (1926).

methanesulfonic acid; and also stated[5] that the reactions of formaldehyde sodium bisulfite indicated the sulfonic acid structure. In 1928 Schroeter and Sulzbacker[6] admitted that these bisulfites could not be esters of sulfurous acid, but held that the sulfonic acid structure was not satisfactory and proposed "polymolecule formulas" of the type $(R_2CO)\cdot(SO_2)\cdot(HOH)$. A more recent investigation[7] confirms the sulfonic acid structure.

Experimental

The aldehyde and ketone bisulfites were prepared by adding freshly purified aldehyde or ketone to an excess of a saturated solution of sodium bisulfite. The crystalline addition product was obtained by cooling the solution and adding alcohol. The compounds were purified by recrystallization.

Near-saturated solutions were made for use in the Raman tube by dissolving the aldehyde or ketone bisulfite in distilled water prepared according to the directions of Ellis and Kiehl.[8]

The apparatus was that described in detail by Houlton and Tartar.[9] The Raman spectra were taken at 60°; the apparatus was not adapted for the use of much lower temperatures. Wave lengths were calculated by use of Hartmann's interpolation formula from the comparator readings of the plates. Three plates were taken of each compound and average values of the three wave lengths used in computing the wave number. Intensities were estimated visually on a basis of ten.

Results

In most cases excellent spectra were obtained. Butyraldehyde sodium bisulfite gave a continuous background which made accurate reading of the plates exceedingly difficult and actually obscured some of the lines of lower frequency. This continuous background is believed to be due to the reversible dissociation of the aldehyde bisulfite into aldehyde and bisulfite, the insoluble aldehyde causing a slight cloudiness in the solution. An excess of sodium bisulfite did not remove the continuous background.

The length of exposure varied with the compound used. In all cases the lines were obtained within a few hours but twenty to thirty hour exposures were taken to be certain that no faint lines were overlooked. Long exposures were of no advantage to those plates in which a continuous background was present. Ten hours was found to be quite sufficient for all the compounds.

The results in terms of wave numbers for the addition products of the first four aldehydes and acetone are given in Table I. The numbers in parentheses are the relative intensities of the lines. Personal errors were eliminated by reading the plates from both directions; the readings were within about two ångströms, which represents an error of about ten wave numbers.

TABLE I

RAMAN FREQUENCIES FOR ALDEHYDE AND KETONE BISULFITES

Substance	Raman shifts
$HCHO\cdot NaHSO_3$	397(5), 518(5), 771(7), 1039(6), 1096(6), 1196(4), 1332(1), 1444(2), 1686(2), 2937(5), 3048(6)
$CH_3CHO\cdot NaHSO_3$	432(2), 628(1), 772(5), 976(6), 1096(1), 1210(2), 1356(1), 1672(2), 3040(5)
$C_2H_5CHO\cdot NaHSO_3$	325(4), 538(3), 781(5), 976(5). 1048(5), 1196(2), 1318(1), 1448(2), 1668(2), 2948(5), 3036(5)
$C_3H_7CHO\cdot NaHSO_3$	781(6), 986(4), 1048(4), 1191(3), 1332(3), 1458(3), 1677(5), 2868(? v.b.) 2929(9), 2977(?), 3052(10)
$(CH_3)_2CO\cdot NaHSO_3$	330(9), 442(2), 548(7), 698(6), 772(6), 840(5), 981(4), 1034(6), 1186(6), 1328(2), 1453(3), 1677(3), 2937(?), 3052(8)

Discussion and Conclusions

The dissolved aldehyde and ketone bisulfites have little effect on the water bands. The band with maximum at 3450 cm.$^{-1}$ was, however, slightly broadened. Raman spectra were also taken of acetone and the first four aldehydes separately and check those of Kohlrausch and Koppl[10] except in the lower regions of the spectrum for formaldehyde, acetaldehyde, and propionaldehyde. In the case of formaldehyde solution three new lines were observed, *viz.*, Δv = 412, 573, and 777 cm.$^{-1}$. In the case of acetaldehyde and propionaldehyde one line appeared that is not previously reported: 772 cm.$^{-1}$ for acetaldehyde and 668 cm.$^{-1}$ for propionaldehyde. We attribute these lines to possible polymerization which takes place on prolonged standing at temperatures higher than room temperature.

To have an adequate basis for discussing the data, there are included in Table II the frequencies which are characteristic of certain types of valence bonds within the molecule. Figure 1 gives a diagrammatic presentation of the data on acetone, the first four aldehydes, and the addi-

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(5) Raschig and Prahl, *Ann.*, **448**, 265–312 (1926).

(6) Schroeter and Sulzbacker, *Ber.*, **61B**, 1616–1627 (1928).

(7) Lauer and Langkammerer, THIS JOURNAL, **57**, 2360 (1935).

(8) Ellis and Kiehl, *ibid.*, **57**, 2145 (1935).

(9) Houlton and Tartar, *ibid.*, **60**, 544–548 (1938).

(10) Kohlrausch and Koppl, *Z. physik. Chem.*, **24B**, 370 (1934).

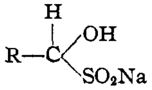
tion products of these compounds with sodium bisulfite. This diagram also includes data on sodium bisulfite by Fadda[11] and on some alkyl sulfonates by Houlton and Tartar.[12]

TABLE II

CHARACTERISTIC FREQUENCIES FOR VARIOUS VALENCE BONDS

Linkage	Characteristic frequency, cm.$^{-1}$			
S—O	340–390	510–560	1030–1050	1140–1180
C—S		670–700	750–790	
C═O				1700–1730
C—H	1450	2862	2930	2970

The possible structures, other than the polymolecule formula, for the aldehyde and ketone bisulfites are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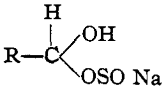
II

From our data the following points are evident regarding these two structures.

(1) A line appears in all the aldehyde and ketone bisulfites at about 770 cm.$^{-1}$. Since a line is present in this region for formaldehyde solution, acetaldehyde and *n*-butyraldehyde, this line has little significance in these cases. It is characteristic of the C–S linkage and occurs in the spectra of propionaldehyde bisulfite but not in that of the pure aldehyde. This indicates the presence of a carbon–sulfur bond in these compounds.

(2) Acetaldehyde and acetone bisulfite gave a line between 650 and 700 cm.$^{-1}$ which does not occur in either of the carbonyl compounds. This is also characteristic of the direct carbon–sulfur linkage.

(3) The frequency characteristic of the carbonyl group, 1720 cm.$^{-1}$, disappears in the bisulfite addition compounds. The line at 1650 cm.$^{-1}$ in all bisulfites and in sulfonates is undoubtedly due to the 1650 cm.$^{-1}$ vibration of water. This indicates that the "polymolecule formula" is unnecessary.

(4) A frequency characteristic of the SO_2 group at 1170 cm.$^{-1}$ and the other frequencies characteristic of the S–O bond are all present.

(5) There is a frequency at about 970 cm.$^{-1}$ which may be due to the C—OH vibration. However, it is difficult to characterize this frequency closely since it is very similar to the C—CH_3 frequency.

(6) It should also be noted that all the aldehydes and acetone give lines around 2720, 2840, and 2900 cm.$^{-1}$ which do not occur in the aldehyde and ketone bisulfites. These are the lower C—H frequencies and are probably changed in the bisulfite addition product by the presence of the sulfonate group.

The presence of a direct C—S bond shows that structure I must be correct. Furthermore, the disappearance of the C═O frequency and the possible presence of a C—OH frequency show that the polymolecular formulas must be incorrect.

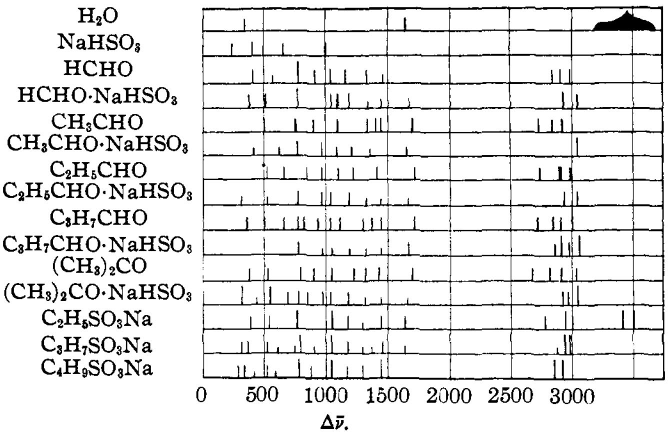

Fig. 1.—Raman spectra of acetone, the first four aldehydes with their sodium bisulfite addition products and some related compounds.

Summary

Raman data have been presented for the bisulfite addition products of the first four aldehydes and acetone.

From these data it has been shown that the structure of the aldehyde and ketone bisulfites is such that there is a carbon–sulfur bond and that there is no necessity for "polymolecule formulas."

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[11] Fadda, *Nuovo cimento*, **9**, 227 (1932).

[12] Houlton and Tartar, THIS JOURNAL, **60**, 544 (1938).