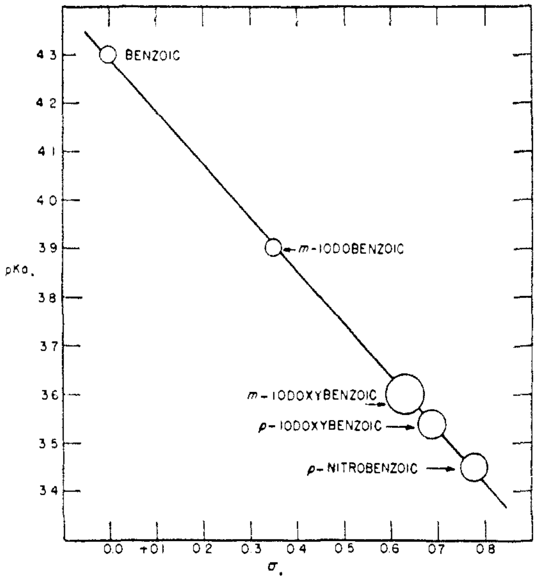

Fig. 2.—Hammett plot of ionization constants of substituted benzoic acids.

These large positive values of the σ constant indicate that the iodoxy group is a strongly electron-withdrawing substituent in either the meta or para position of the benzene nucleus and is comparable in this respect with the nitro-, cyano- and benzeneazo-groups. It is of interest to compare the values of σ for the iodoxy substituent with those for the nitro substituent. The nitro substituent has a slightly greater electron withdrawing power in the meta position ($\sigma = +0.71$), and in the case of the para substituents when compared for derivatives other than anilines and phenols ($\sigma = +0.78$). In nitroaniline and *p*-nitrophenol reactions, it is presumably the involvement of the reacting center in the resonance of the molecule which is the cause of the anomalous higher σ value ($\sigma = +1.27$). The fact that the iodoxy group directs electrophilic substitution in the benzene ring more exclusively meta than does the nitro group[13] may be rationalized on the following basis. The competitive rates of substitution in the meta position are expected to be roughly the same, the rate with iodoxybenzene perhaps being slightly faster. The rate of para-substitution in iodoxybenzene is expected to be considerably slower than in nitrobenzene because of the large electrostatic repulsion between the center of positive charge located at the iodine in the iodoxy group and at the adjacent ring carbon of the activated complex for para-substitution, and the consequent high energy of the latter. Thus the *ratio* of meta to para-substitution in iodoxybenzene would be larger than the corresponding ratio in nitrobenzene. An explanation of the meta-directing influence of the $-N(CH_3)_3^+$ group based on the same considerations has been suggested by Roberts, *et al.*[14]

The working hypothesis of a large positive charge on iodine in the iodoxy group is thus supported by the properties of the material (high-melting, low solubility in water, but less in non-polar solvents, indicating a large internal dipole), previous observations of the chemical reactions,[3] and is supported by the results here reported.

(13) J. Masson, E. Race and F. Pounder, *J. Chem. Soc.*, 1669 (1935).

(14) J. D. Roberts, P. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951).

UPTON, L. I., N. Y.

[COMMUNICATION NO. 1480 FROM THE KODAK RESEARCH LABORATORIES]

Rearrangement Peaks in the Mass Spectra of Certain Aliphatic Acids

BY G. P. HAPP AND D. W. STEWART

RECEIVED FEBRUARY 13, 1952

Purified samples of formic, acetic, propionic, *n*-butyric, isobutyric, *n*-valeric, isovaleric, acrylic, vinylacetic and isocrotonic acids have been examined in a sector-type mass spectrometer, and normalized spectra tabulated. C^{13}-Carboxyl labeled *n*-butyric acid has also been examined in view of the rearrangement peak at mass 60, which is the principal peak in *n*-butyric, *n*-valeric and isovaleric acids. Results in *n*-butyric acid show that the carboxyl group is quantitatively retained in this rearranged ion, suggesting a simple hydrogen transfer as the most probable mechanism of formation. Other rearrangement peaks are noted.

The mass spectrum of formic acid has been studied in detail by Mariner and Bleakney,[1] and spectra of formic, acetic, propionic and *n*-butyric acids have been recorded in the American Petroleum Institute (A.P.I.) series of reference spectra.[2] In the present work, purified samples of these and six other aliphatic acids have been examined in a mass spectrometer, with particular attention to those peaks which can be due only to molecular rearrangement, and not to any combination of bond cleavages, during the ionization and dissociation process.

As might be expected, the published spectra for formic acid do not agree with each other, nor with our results, since ionizing conditions and method of scanning were presumably quite different in the three instruments. Our values for masses 44 and 28 are especially high for this compound. A similar comparison of our spectra of acetic, propionic and *n*-butyric acids with the A.P.I. data also shows expected variations. Agreement is best in the case of *n*-butyric acid, especially in the mass range from 88 down to 60. Such comparisons of mass spectra obtained on instruments of different design can seldom be made directly, but this does not lessen the validity of comparisons between the spectra of related compounds obtained with a single instrument under constant operating conditions, as in the present work.

In the usual picture of ionization by electron im-

(1) T. Mariner and W. Bleakney, *Phys. Rev.*, **72**, 792 (1947).

(2) *Catalog of Mass Spectral Data*, Amer. Pet. Inst. Res. Proj. 44, Nat. Bur. Stds., Washington, D. C., Series Nos. 300, 301, 302, 303.

pact, it is assumed that the energy imparted to the molecule may raise it to an excited vibration state, above the dissociation limit for a particular configuration of atoms. This is immediately followed by cleavage of one or more valence bonds, giving rise to fragments which may be neutral or variously charged. Because of the low pressures existing in the ionization region (10^{-4} to 10^{-5} mm.), it must be further assumed that secondary reactions between these fragments are so unlikely that they can be neglected.

Rearrangement peaks cannot be formed by such a simple process. The mechanism of their formation is not well understood. Stevenson and Hipple,[3] in studying the dissociation products of isobutane, ascribed the rearrangement yielding a $C_2H_5^+$ ion to an initial isomerization followed by the reaction

$$n\text{-}C_4H_{10} \longrightarrow C_2H_5 + C_2H_5^+ + e^-$$

The observed minimum energy for electrons to produce this reaction excluded alternate mechanisms involving the shift of one hydrogen atom, with the formation of CH_3 and CH_2 fragments. A difference of 0.7 e.v. for the appearance potential of $C_2H_5^+$ in *n*- and isobutane was suggested as being associated with the activation energy of the isomerization. Honig[4] has also studied this reaction, using C^{13}-labeled isobutane, and has reached similar conclusions.

Rearrangement peaks in hydrocarbons and oxygenated compounds have been observed and discussed by Langer.[5] Several possible mechanisms are offered, including (1) isomerization, (2) a migration of binding electrons, resulting in a shift of hydrogen atoms around the skeleton of the molecule, or (3) a more complicated form of regrouping where a molecule loses its structural identity in the excited state, so that a random recombination into fragments may occur. The authors could not account for all of their observations on the basis of any one of these possibilities. In studying the unusually large rearrangement peak of 2,2-dimethylpropane at mass 29, using this compound terminally labeled with C^{13}, Langer and Johnson[6] support the theory of statistical rearrangement of ionic fragments, or randomization in the excited molecule.

In much of the preceding work, the rearrangement peaks were small and represented modes of dissociation much less probable than straightforward bond cleavages. The present work on some of the aliphatic acids points out numerous rearrangement peaks. Of these, the mass 60 peak of *n*-butyric acid, which is the largest peak in the entire spectrum, was selected for more detailed study by observing the mass spectrum of the acid in which the carboxyl carbon contained 51.5 atom per cent. C^{13}. The experimental results on this peak do not support the explanations that fit the cases of isobutane and 2,2-dimethylpropane, as cited above.

Results

The mass spectra of the ten acids of ordinary isotopic composition are shown in Table I, with the largest or base peak in the spectrum assigned an arbitrary value of 100. For comparison of different acids, the last line in the table gives the sensitivity of the base peak in divisions per micromole of sample admitted from a calibrated micropipet. Normalized peaks smaller than 1.0 have been omitted as of doubtful significance. A sizable background peak in the present mass spectrometer at mass 28 (and smaller peaks at masses 18 and 44) make the recorded values at these points in the spectra less accurate, even though suitable corrections have been included for all background peaks observed before introduction of the sample.

Forty-six peaks due principally to rearrangement processes are identified in Table I by the letter R. The contribution due to heavy isotopes in nonrearranged ions is small in most cases. Of the rearrangement peaks, 36 are associated with masses 18, 30, 31, 46 and 60, where nearly all of the acids show significant peaks. Those at mass 18 are undoubtedly due to the H_2O^+ ion, which can be formed from the acids only by rearrangement. Since the presence of a trace of water in the acids cannot be excluded, and since background effects may also influence this mass, no detailed study has been made of these peaks.

The peaks at masses 30 and 31 (all relatively small) are presumably due to ions of the forms CH_2O^+ (or $CHOH^+$) and CH_3O^+ (or CH_2OH^+). In the case of mass 30, doubly charged ions of mass 60 also cannot be excluded, nor can $C_2H_6^+$ ions formed by a more complicated type of rearrangement in the heavier acids. Similar considerations apply to the observed peaks at mass 46, where the largest peak due to a rearrangement is less than 3% of the base peak. Ions of the form $CH_2O_2^+$ (as $HCOOH^+$) or $C_2H_6O^+$ (as $C_2H_5OH^+$) would account for this mass.

At mass 60, the situation is somewhat different. Here, three of the acids (*n*-butyric, *n*-valeric and isovaleric) rearrange to give the largest peaks in their spectra, while two others (vinylacetic and isocrotonic) give smaller but significant peaks. From the C_4 acids, the fragment of mass 60 might be either $C_2H_4O_2^+$ (as CH_3COOH^+) or $C_3H_8O^+$ (as $C_3H_7OH^+$). For valeric acid, there is the additional possibility of C_5^+, but this can be dismissed on the basis of other mass spectrometric experience, where such highly stripped groups of carbon atoms are uniformly rare. Understanding the mass 60 rearrangement in *n*-butyric acid therefore depends on learning whether a C_2H_4 group or a CO group is eliminated from the parent molecule. The former will lead to a residual fragment corresponding to acetic acid, the latter to propyl alcohol, also of mass 60.

To differentiate between these two possibilities, *n*-butyric acid was prepared containing 51.5 atom per cent. C^{13} in the carboxyl group. When this acid was admitted to the spectrometer, the spectrum obtained was a composite of 48.5% of the ordinary acid and 51.5% of the pure C^{13}-acid. From the observed spectra of the enriched and the

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(3) D. P. Stevenson and J. A. Hipple, Jr., THIS JOURNAL, **64**, 1588 (1942).

(4) R. E. Honig, *Phys. Rev.*, **75**, 1319 (A) (1949).

(5) A. Langer, *J. Phys. Colloid Chem.*, **54**, 615 (1950).

(6) A. Langer and P. Johnson, Paper before Symposium on Isotopes in Petroleum Chemistry, Amer. Chem. Soc., Chicago, Ill., September, 1950.

TABLE I

NORMALIZED MASS SPECTRA OF ALIPHATIC ACIDS

A, estimated peak height after correction for $(Hg^{204})^{++}$; R, indicates peaks due principally to rearrangement processes.

m/e	Formic acid	Acetic acid	Propionic acid	n-Butyric acid	Isobutyric acid	n-Valeric acid	Isovaleric acid	Acrylic acid	Vinyl acetic acid	Isocrotonic acid
12	6.0	4.3	2.0	1.6	1.9	3.4	4.3	3.6	4.1	4.6
13	1.5	7.4	1.4	1.0		2.5	2.8	3.0	1.8	3.6
14		20.3	3.4	3.2	1.8	4.4	5.7	3.4	3.8	4.6
15		38.8	3.6	6.6	6.8	9.2	11.8	2.4R	6.2R	7.8
16	9.2	7.0	1.5	1.7	1.8	3.4	4.7	2.1	2.8	3.6
17	7.9	4.2	3.2	2.5	2.5	4.6		2.4	3.3	2.1
18	26.3R	9.8R	11.3R	8.3R	9.4R	11.9R		5.6R	11.2R	17.7R
24								3.0	1.1	
25		1.9	4.2	1.4	1.8	2.3	3.6	13.3	3.1	6.0
26		1.6	25.2	9.6	9.4	14.2	10.7	60.6	10.7	14.0
27			56.5	46.2	47.4	58.0	54.0	*100.0*	22.1	22.0
28	83.3	42.6	*100.0*	36.8	39.9	64.7	82.2	64.5	66.3	73.8
29	*100.0*	17.1	55.6	21.7	11.1	39.4	32.5	9.3	10.4	14.7
30	1.9		8.8R	1.1R		2.3R	1.6R		1.7R	1.8R
31		4.9R	4.0R	3.1R	1.8R	4.8R	5.9R		2.8R	8.0R
36				1.6	1.0	2.3	3.6	1.1	4.0	5.8
37				3.8	5.1	4.1	5.9	1.4	15.8	18.4
38				6.2	7.7	7.3	10.2		23.1	28.9
39				26.8	32.9	40.1	52.8		*100.0*	*100.0*
40		1.8		4.5	6.4	6.4	9.0		24.0	28.0
41		7.3	1.6	34.1	65.3	60.6	85.1	2.2	85.8	62.8
42		25.7	3.6	35.5	16.0	27.5	30.1	2.3	45.7	21.6
43		*100.0*	2.4	23.3	*100.0*	35.6	60.2	8.3R	12.0	11.0R
44	91.1	9.1	5.7	6.4	10.7	13.3	17.8	29.6	24.4	18.1
45	45.9	88.4	33.9	23.7	18.1	29.4	34.4	32.8	28.3	23.9
46	57.1	1.1	2.7R	1.2R		2.3R	1.2R	2.2R		2.0R
47			1.6R							
48						2.3				
49										1.8
50						1.8	2.4			
51						3.4	3.1			
52						1.2	1.2	1.3		
53			1.6		1.3	5.0	4.5	6.1	1.5	4.4
54						2.8	1.2	1.9		
55			10.0	15.4	7.8	23.2	11.4	57.1	2.0	6.0
56			11.1		1.0	9.9	8.8	2.3		
57			13.8			10.8	11.4		6.5	4.4
58									22.9	1.4
59					1.1R	3.0	4.7			
60		45.1		*100.0R*	1.8R	*100.0R*	*100.0R*		4.2R	13.3R
61		1.1		2.5		4.8	6.6			
68									9.2	38.1
69				2.3		5.7	11.4		5.0	19.8
70				3.5	3.2	1.8	1.6			2.8
71				2.7	2.7		1.2	3.4	1.4	8.2
72								61.6		
73			18.5	31.6	29.7	29.8	8.3R	2.4		3.9R
74			27.7	1.2	1.1	14.0R	14.2R			
75			1.1							
83						2.8				
84						1.2	3.1			
85							1.9		2.0	2.1
86						8.7			20.5	42.4
87				1.3		1.6	16.6		1.0	2.3
88				2.3	6.7		1.6R			
102						(1.8)A	(3.3)A			
Sensitivity	1.28	1.53	2.12	1.89	2.35	1.64	1.60	1.47	1.58	1.38

ordinary materials, a calculated spectrum was obtained for the pure *n*-butyric acid-1-C^{13} with C^{12} and C^{13} in the ordinary ratio in all positions except the carboxyl group. Its spectrum, and that of ordinary butyric acid, are given in Table II.

From Table II the most abundant fragment of

TABLE II

NORMALIZED SPECTRA OF ORDINARY AND C^{13}-CARBOXYL-LABELED *n*-BUTYRIC ACIDS

R, indicates peaks due principally to rearrangement processes.

m/e	*n*-Butyric acid	*n*-Butyric acid-1-C^{13}	*m/e*	*n*-Butyric acid	*n*-Butyric acid-1-C^{13}
12	1.6	....	42	35.5	10.8
13	1.0	1.4	43	23.3	40.1
14	3.2	2.6	44	6.4	7.3
15	6.6	5.3	45	23.7	8.4
16	1.7	1.6	46	1.2R	19.4
17	2.5	1.6	55	15.4	...
18	8.3R	5.9R	56	...	15.2
25	1.4	1.3	60	*100.0R*	...
26	9.6	8.8	61	2.5	*100.0R*
27	46.2	43.6	62	...	1.4
28	36.8	29.6	69	2.3	...
29	21.7	27.2	70	3.5	2.1
30	1.1R	2.8	71	2.7	3.2
31	3.1R	2.7R	72	...	2.6
36	1.6	...	73	31.6	...
37	3.8	3.2	74	1.2	31.4
38	6.2	5.8	87	1.3	...
39	26.8	25.6	88	2.3	1.5
40	4.5	4.5	89		2.3
41	34.1	32.0	Sensitivity	1.89	1.77

the C^{13} compound is mass 61, and the intensity ratio of this peak to peaks at masses 74 and 89 is almost precisely that which exists between mass 60 and masses 73 and 88 in the ordinary material. We conclude that the carboxyl carbon is completely retained in the rearranged fragment. Barring the unlikely possibility that the molecule is scrambled in a unique manner so that one of the chain carbons is eliminated simultaneously with a single oxygen atom from the carboxyl group, this supports the mechanism by which a C_2H_4 group is eliminated, with the shift of a hydrogen atom to the remaining $-CH_2COOH$ fragment. Excluded is any general randomization of bonds within the molecule or any isomerization, as this term is usually understood.

Isobutyric acid (Table 1) shows less than 2% of the probability for rearrangement to mass 60 shown by *n*-butyric acid. This would appear to be connected with the fact that the α-carbon now requires the transfer of two hydrogen atoms from adjacent groups instead of only one. However, similar reasoning fails when based on the unsaturated C_4-isomers, vinylacetic and isocrotonic acids. In isocrotonic acid, two hydrogen atoms must be transferred and a double bond broken, while only one hydrogen need be shifted in vinylacetic acid; yet the former shows a 3-fold greater probability of rearrangement. It is possible that this arises from the existence of conjugated double bonds in the isocrotonic acid, but the matter has not been further investigated since the rearrangement peaks are relatively small in both compounds.

Two additional factors were investigated which might be expected to affect the probability of rearrangement in *n*-butyric acid. The energy of the ionizing electrons was varied from 27 to 150 volts, while the electron current was held constant. This produced a variation in all observed peak heights, but the ratio of mass 60 to other peaks was essentially constant over the entire range. It was not possible to reduce the electron energy below 27 volts with the emission regulator circuit available, so no appearance potentials were measured.

In a parallel experiment, the temperature of the envelope surrounding the ion source was varied from 30 to 73°, and then to 125°. All of the larger peaks in the *n*-butyric acid spectrum, including mass 60, showed an increase of from 30 to 50% between 30 and 73°. From 73 to 125°, the mass 60 peak increased an additional 7%, while the parent peak, at mass 88, decreased about 10% and other peaks remained essentially constant. Since actual temperatures in the ionizing region were not measured, no conclusions can be drawn except that the rearrangement does not appear to be highly sensitive to temperature.

Experimental

The mass spectrometer was of the 60° sector-type,[7] and was constructed in these Laboratories. The ionizing potential was held at 90 volts, and the ion-accelerating potential was held at 1700 volts. Automatically controlled magnetic scanning was used while the peaks were recorded on a Leeds and Northrup Speedomax G recorder. Sensitivity factors up to 50 were controlled manually at both the electrometer input and the recorder input. The ion-source temperature was not controlled, although the temperature of the envelope was varied, as noted in some experiments.

TABLE III

ACIDS USED IN THE INVESTIGATION

Acid	Obsd. b.p., °C.	Pressure, mm.	Obsd. n^t_D	*t*, °C.
Formic	M.p. 6–8°		....	...
Acetic	118.5	Atm.	1.3713	25
Propionic	141.1	Atm.	1.3852	25
n-Butyric	163.7	Atm.	1.3961	25
n-Butyric-1-C^{13}[a]	161.5–162.5	754	1.3985	20
Isobutyric	84.8–85.1	50	1.3922	25
n-Valeric	187	Atm.	1.4048	25
Isovaleric	175	Atm.	1.4019	25
Acrylic	47, f.p. 13.9	14	....	...
Vinylacetic[b]	31	0.5	1.4211	25
Isocrotonic[c]	72–73	15	1.4411	20

[a] The C^{13}-labeled acid was prepared by E. C. Armstrong by the carbonation of *n*-propylmagnesium bromide with CO_2 containing 51.5 atom per cent. C^{13}. The procedure and apparatus were similar to those described by M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich in "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949. The acid was isolated in almost quantitative yield as the sodium salt, from which the free acid was obtained by treatment with 85% phosphoric acid and distillation through a Drierite column under a pressure of about 0.001 mm. The sample was characterized by redistillation under atmospheric pressure and by refractive index measurements. [b] The vinylacetic acid was prepared by James VanAllan according to the procedure given in "Organic Syntheses," 24, 96 (1944). [c] Isocrotonic acid was prepared by Gerhard W. Leubner. β-Chloroisocrotonic acid was obtained by the reaction of ethylacetoacetate with phosphorus pentachloride and reduced by sodium amalgam as described by A. Michael and O. Schulthess, *J. prakt. Chem.*, [2] **46**, 236 (1892), with modifications by H. Scheibler and J. Voss, *Ber.*, **53**, 379 (1920), and E. L. Skau and B. Saxton, THIS JOURNAL, **50**, 2693 (1928).

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(7) A. O. Nier, *Rev. Sci. Instruments*, **18**, 398 (1947); R. L. Graham A. L. Harkness and H. G. Thode, *J. Sci. Instruments*, **24**, 119 (1947).

Samples were admitted by a calibrated micropipet, using the technique described by Taylor and Young.[8] Sample pressures were computed to be between 5 and 50 × 10^{-3} mm. at the capillary leak, which was located inside the ion source.

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(8) R. C. Taylor and W. S. Young, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 811 (1945).

Samples of the acids used had boiling points and refractive indices as shown in Table III. The formic acid was Eastman Kodak Co. white label material, not further purified. We are indebted to C. F. H. Allen and L. B. Genung, for arranging for the other purifications and syntheses.

Rochester, N. Y.

[Contribution from the National Research Council (Canada)]

The Infrared and Raman Spectra of *p*-Dioxane

By F. E. Malherbe[1] and H. J. Bernstein

Received December 26, 1951

The infrared spectrum of liquid *p*-dioxane has been obtained from 2.5–37 μ and three new fundamentals were observed. Reinvestigation of the Raman spectrum gave one new fundamental. A tentative assignment of all vibrational modes has been made and the specific heat calculated at several temperatures.

In the course of investigating complex formation with *p*-dioxane by spectroscopic methods we obtained the infrared spectrum of *p*-dioxane in the liquid, solid and gas phase and the Raman spectrum of the liquid. The infrared spectrum of the liquid and gas had been obtained previously[2,3] from

Table I

Assignment of the Fundamentals in *p*-Dioxane

		Description of vibration	This work	Burket[a] and Badger	Ramsay[b]
A_g	ν_1	CH stretching	2966		
	ν_2		2855		
	ν_3	Deformation	1443		
	ν_4	Twisting	1303	1305	
	ν_5	Wagging	1127		
	ν_6	Rocking	852		
	ν_7	Ring stretching	1015	1014	1111
	ν_8		834	835	835
	ν_9	Ring bending	433		485
	ν_{10}		422		(390)[c]
B_u	ν_{11}	CH stretching	2967		
	ν_{12}		2860		
	ν_{13}	Deformation	1446		
	ν_{14}	Twisting	1368		
	ν_{15}	Wagging	1251	1253	
	ν_{16}	Rocking	887		
	ν_{17}	Ring stretching	1120	1122	1020
	ν_{18}	Ring bending	610		740[d]
	ν_{19}		273		233[c]
A_u	ν_{20}	CH stretching	2921		
	ν_{21}		2899		
	ν_{22}	Deformation	1446		
	ν_{23}	Twisting	1318		
	ν_{24}	Wagging	1286	1285	
	ν_{25}	Rocking	1046		
	ν_{26}	Ring stretching	1081	1086	1136
	ν_{27}		874	874	879 or 889
	ν_{28}	Ring bending	283		
B_g	ν_{29}	CH stretching			
	ν_{30}				
	ν_{31}	Deformation	1461		
	ν_{32}	Twisting	1396		
	ν_{33}	Wagging	1216		
	ν_{34}	Rocking	946		
	ν_{35}	Ring stretching	1109	1109	1125
	ν_{36}	Ring bending	486		433

[a] Reference (3). [b] Reference (2). [c] Calculated in reference (2) from a normal coördinate treatment of the skeleton. [d] Observed as weak band and matched with the calculated value of 742 cm.$^{-1}$. The observed band is very strong, however, and is at 610 cm.$^{-1}$.

Table II

Raman Spectrum of Liquid *p*-Dioxane

νcm.$^{-1}$ [a]	Relative[a] intensity	Polarization[b]	This research νcm.$^{-1}$	Int.	Assignment[c]
178[d]	0				
241[e]	1				
			422	1	ν_{10} A_g
433[f]	2	p	433	2	ν_9 A_g
486	4	d	486	4	ν_{36} B_g
835	8	p	834	8	ν_8 A_g
850	1	d	852[h]	1	ν_6 A_g
946	1	d	946	1	ν_{34} B_g
1014	6	p	1015	6	ν_7 A_g
1109	3	d	1109	3	ν_{35} B_g
1125	3	p	1127	3	ν_5 A_g
1209[g]	1	d			
1222	5	d	1216	5	ν_{33} B_g
1305	8	p	1303	8	ν_4 A_g
1330	2	p	1334	2	$\nu_{25} + \nu_{28}$ A_g
			1396	1	ν_{32} B_g
1448	8	p	1443	8	ν_3 A_g
1455	2	d	1461	2	ν_{31} B_g
2662	0	p	2662	1	$\nu_3 + \nu_{33}$ A_g
2720	1	p	2720	1	$\nu_{22} + \nu_{24}$ A_g
2748	3	p	2748	2	$\nu_3 + \nu_4$ A_g
2854	8	p	2855	8	ν_2 A_g
2890	2	p	2889	2	$2\nu_3$ A_g
2966	10	p	2966	10	ν_1 A_g
3064	1	p			ν_{29} B_g ?

[a] Summary of results of eight authors given by K. W. F. Kohlrausch in "Ramanspektren." [b] Polarization measurements are by B. Saksena, *Proc. Ind. Acad. Sci.*, **12**, 321 (1940). [c] This work. [d] Obtained only by J. Lecomte, *J. chim. phys.*, **33**, 626 (1936). [e] Obtained by Venkateswaran, *Proc. Ind. Acad. Sci.*, **2**, 279 (1935), and Saksena, reference (b). [f] Observed as double; A. Simon and F. Feher, *Ber.*, **69**, 214 (1936). [g] Our Raman spectrum contains a band at ~ 1200 cm.$^{-1}$ corresponding to the band at 1209 cm.$^{-1}$ which we are certain is ν_1 excited by λ 4047. [h] This band is assigned as of species A_g although it is given as depolarized. However, it is not impossible that the depolarization of such a weak band has been estimated incorrectly.

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