no effect of the distance of the reacting group from the charge could be found for the four homologous ions.

3. The kinetic salt effect for the saponification of the betaine ester was studied down to ionic strength 0.0001 and was found to be that given by the Brönsted–Debye equation for values of $\sqrt{\mu}$ below 0.1.

4. Calculations were introduced to show how certain deviations from second order can lead to an apparent negative kinetic salt effect, and an attempt was made to show how such deviations could account for certain previously reported kinetic salt effects in the opposite direction from that expected from Brönsted's theory.

COPENHAGEN, DENMARK RECEIVED OCTOBER 17, 1935

[CONTRIBUTION FROM THE GOODYEAR TIRE & RUBBER COMPANY]

Raman Spectrum of Rubber and Some Related Hydrocarbons

BY S. D. GEHMAN AND H. J. OSTERHOF

The Raman spectra of organic compounds have been used very extensively in studying their structure and the method has been applied for the solution of some difficult problems of constitution. The extension to highly polymerized materials has been very limited, although it offers a means of gaining information about the primary chemical linkages without disturbing the secondary forces. Signer and Weiler[1] showed that polysterol gave a strong line spectrum in which the frequencies were practically identical with those of ethylbenzene, the unit of structure in the long chain molecules. They showed, furthermore, that the frequencies were the same in the solid state and in solution, for this polymer, indicating an independence from the micellar forces.

The Raman spectrum has not been used at all, previously, for the study of rubber or related high polymers, attempts to secure a line spectrum leading only to bands and background.[2,3,4] The difficulties and ambiguities in the deduction of the original structure of rubber from chemical reactions should make welcome any insight which can be gained by the application of this newer method.

The Raman spectra of series of organic compounds show that certain frequencies can be ascribed to the various primary organic linkages. Some of these frequencies are remarkably independent of the rest of the structure of the molecule. This property renders possible the use of the Raman spectrum to study the primary linkages in highly polymerized materials, since the frequency will depend not upon the size of the molecule but upon the unit of structure. The various linkages can then be identified by comparison with those of simpler, related structures.

The results to be obtained from a study of the Raman spectra of such materials as rubber and its derivatives promise to be extremely interesting, but the work has been hampered by the presence of a continuous background which we have not been able to eliminate entirely. Signer and Weiler[1] have mentioned the possibility that each molecule of a high polymer possesses a fluorescent end group and have even suggested the measurement of the continuous background intensity as a means for estimating the average molecular size. They admitted, however, as an equally probable alternative, that the background might be caused by fluorescent impurities. It would be interesting to determine for rubber, with the fluorescence microscope, whether the fluorescence occurred in the sheath of the latex particle. Another difficulty encountered in this work is the almost necessary limitation of having to work with solutions and gels thus reducing the Raman intensities due to the dilution. Crystal powder methods[5] might be applicable but they do not seem very promising unless the source of light is entirely free of a continuous spectrum.

Apparatus and Method

The apparatus was of the conventional type for Raman studies of liquids and is sketched in Figs. 1 and 2. The light source was a quartz mercury arc and the spectrograph a Bausch and Lomb No. 2700 constant deviation instrument. The cells were constructed from Pyrex tubing as shown in Fig. 1, having rubber packing at the ends overlaid with a thin coating of acid-proof cement. The arc

---

(1) Signer and Weiler, *Helv. Chim. Acta*, **15**, 649 (1932).

(2) Franklin and Laird, *Phys. Rev.*, **36**, 147 (1930).

(3) Busse, *J. Phys. Chem.*, **36**, 2862 (1932).

(4) Gehman, THIS JOURNAL, **57**, 1382 (1935).

(5) Kohlrausch, "Der Smekal Raman Effekt," Verlag Julius Springer, Berlin, 1931, p. 37.

was cooled by a fan. The equipment was designed for continuous operation and exposure times varied from four to forty-eight hours. In practically all of the work, the filter was an alcoholic solution of Victoria blue dye, as recommended by Magat.[6] It was absolutely necessary to exclude the ultraviolet light and this filter had the added advantage of reducing the intensity of the continuous spectrum from the arc since it transmits almost exclusively the 4358 Å. triplet. This simplifies the interpretation of the results. The filter necessitates much longer exposures than would otherwise be necessary.

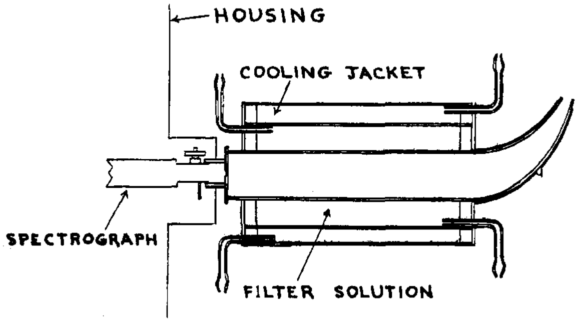


Fig. 1.

Eastman Spectroscopic Plates, type I or II, usually with J green sensitization, were used. The plates were measured with a micrometer microscope especially adapted for use at low magnifications. A calibration curve was drawn for the instrument by measuring the distance of known Raman lines from the 4916 Å. mercury line. Unknown frequencies were then determined by measurement of their distance from this line, a type of procedure recommended by Kohlrausch[5] (p. 43).

The rubber was diffusion rubber prepared by allowing acetone-extracted pale crepe to stand in contact with ethyl ether or petroleum ether for several weeks, precipitating the material in solution with acetone and drying in vacuum. The petroleum ether diffusion rubber gave a much clearer solution in carbon tetrachloride than the ethyl ether diffusion rubber and hence was preferable for this work. However, a mixture of carbon bisulfide and carbon tetrachloride having a refractive index about the same as that of rubber gave a very clear solution with the ethyl ether diffusion rubber so that Raman lines could readily be obtained with it. As it was desirable to obtain as clean and concentrated a solution as possible, the following technique was used in preparing the cells. The diffusion rubber was gathered up with a glass rod as it was precipitated and packed as tightly as possible into the cell. The cell was evacuated until the rubber was solvent-free and the window then sealed on with water-glass. This procedure reduces the handling of the rubber, and consequently the contamination with dust, to a minimum. The rubber was also sometimes dried, cut into small pieces and packed into the cell, being handled with glass rods and forceps. The solvent was introduced by connecting the horn of the cell first to a high vacuum pump and evacuating for several hours and then to a glass tube, the tip of which was broken under the solvent. The solvent flowed in and filled the cell. In this way, concentrations of rubber as high as 40% or more by volume could be obtained.

The balata was purified by dissolving the crude material in hot high test gasoline and, after standing overnight in a tall graduate, siphoning off the solution and centrifuging. It was precipitated by chilling, redissolved in hot petroleum ether, precipitated again by chilling, washed with acetone using a suction filter and dried in vacuum. The cells were prepared in the same way as those for rubber.

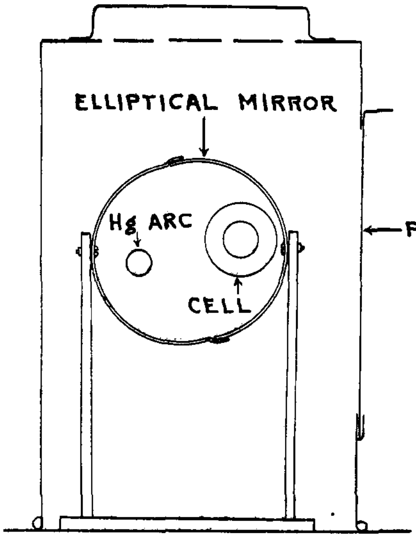


Fig. 2.

Measurements

The Raman frequencies for rubber, balata and myrcene are shown in Fig. 3, the height of the lines indicating the estimated relative intensities. The sample of myrcene was very kindly supplied by Dr. S. Palkin of the Bureau of Chemistry and Soils.[7] It was apparently very pure and showed little background. The lines for trimethylethylene, isoprene and limonene were available in the literature,[8,9,10,11] but these compounds were measured again to check our calibration.

Table I lists the frequencies for these hydrocarbons. The spectra for rubber and balata are still undoubtedly incomplete due to the obscuring of weak lines by the background and the possible coincidence of lines with lines of the solvent, carbon tetrachloride and carbon bisulfide.

In addition to the frequencies listed for trimethylethylene, we found frequencies of 1214, 1150 and 1097 which are not reported by Bourguel and Piaux. Our material was a commercial

---

(6) Magat, *J. phys. radium*, [7] **5**, 347 (1934).

(7) Palkin and Wells, THIS JOURNAL, **55**, 1549 (1933).

(8) Bourguel and Piaux, *Bull. soc. chim.*, **51**, 1041 (1932).

(9) Dadieu and Kohlrausch, *J. Opt. Soc. Am.*, **21**, 286 (1931).

(10) Dupont, Daure and Lévy, *Bull. soc. chim.*, **51**, 921 (1932).

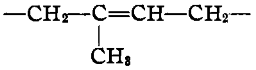
(11) Bonino and Cella, *Mem. accad. Italia Chim.*, **2**, No. 4, 5 (1931).

TABLE I

Raman Frequency	Intensity	Frequency[8]	Intensity	Frequency	Intensity
Isoprene[8]		Trimethylethylene		Limonene[10]	
286	2			308	1
423	3	253	1	330	2
529	6	389	3	350	1
778	3	444	7	432	2
901	5	528	5	471	1
952	6	767	6	491	2
992	3	803	1	524	4
1070	6	1338	4	545	2
1296	8	1446	4	639	2
1388	2	1679	7	662	1
1426	8	2732	1	702	2
1640	15	2861	1	757	10
2864	1	2885	10	790	4
2908	2	2922	1	800	4
2930	2	2973	15	895	3
2986	2	3055	15	918	2
3012	8	Rubber		956	1
3090	5			995	1
		402	1	1020	2
Myrcene		660	1	1054	2
330	5	860	1	1080	3
403	1	910	1	1115	3
456	1	938	1	1155	5
525	1	1017	1	1205	1
587	1	1105	1	1293	2
667	2	1220	1	1311	2
735	1	1302	1	1334	2
805	1	1379	7	{1368 1380}	5
899	3	1446	7		
952	1	1670	15	1397	2
1003	1	2915	9	{1436 1456}	15
1059	2	Balata			
1103	1	534	1	1647	15
1148	1	590	1	1668	15
1190	1	910	1	2834	2
1233	1	1002	2	2856	1
1292	8	1027	2	2881	3
1330	1	1101	2	{2908 2924}	4
1381	6	1250	1		
1424	6	1327	1	2964	2
1454	6	1377	1	3048	2
1636	15	1441	1		
1675	8	1670	15		
2852	6	2914	10		
2913	12				
2965	2				
3004	6				
3083	6				

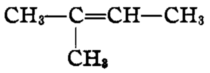
sample which we purified by distillation with a Widmer column and treatment with activated charcoal. The relative intensity of the above lines was not altered appreciably by the purification. The fraction used came over between 36.7 and 37.8° and had a refractive index of $n^{19}D$ 1.3870. These constants are in good agreement with those of Bourguel and Piaux. It is possible, however, that the above frequencies may be due to traces of allenic impurities in our trimethylethylene, since the strongest lines for methyl-, propyl- and butylallene correspond rather closely to the above frequencies.

The generally accepted structural formulas are as follows.[12]



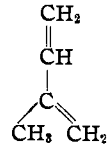
$-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-$

Rubber

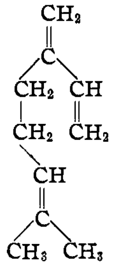


$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3$

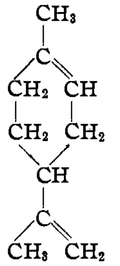
Trimethylethylene



Isoprene



Myrcene



Limonene

Balata is regarded as a *trans* form of the chain of which rubber is a *cis* form.

In comparing these structures, it will be noted that the double bond in trimethylethylene connects the same general structure as in rubber and balata. There is also a bond of this type in myrcene and likewise in the ring of limonene. The Raman frequency for this linkage for trimethylethylene is 1679 cm.$^{-1}$ as compared to 1670 for rubber, 1670 for balata, 1675 for myrcene and 1668 for limonene. The differences are scarcely larger than experimental errors but nevertheless the value for trimethylethylene appears to be somewhat larger than that for the others. Everything considered, this frequency is remarkably constant. The correspondence between the spectrum of rubber and that of trimethylethylene is not nearly as close as that shown by Signer and Weiler to exist between ethylbenzene and polysterol.

The double bonds in isoprene have a single Raman frequency of 1640 cm.$^{-1}$, a value distinctly lower than that for the bonds of the trimethylethylene type. Myrcene has two double bonds similar to the isoprene bonds, in fact a myrcene molecule can be regarded as an isoprene unit joined to a trimethylethylene unit. The exter-

---

[12] Egloff, Herrman, Levinson and Dull, *Chem. Rev.*, **14**, 287 (1934).

nal double bond of limonene is also similar to an isoprene bond. Hence we find in the Raman spectrum of myrcene a line of frequency 1636 cm.$^{-1}$ of about twice the intensity of the 1675 frequency. Limonene shows lines of frequencies 1647 and 1668 of equal intensity.

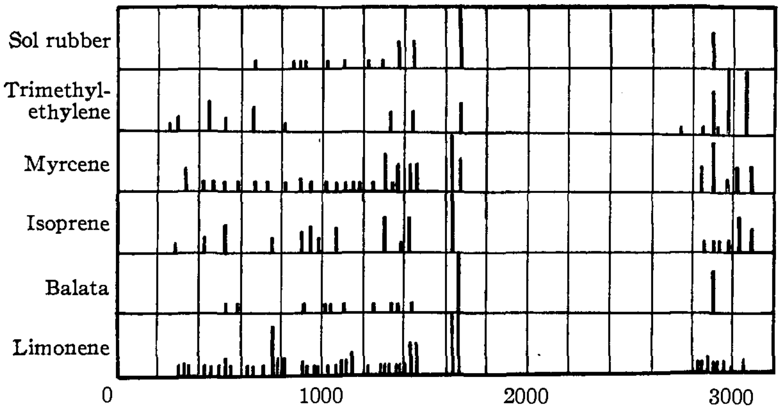


Fig. 3.

The frequencies for myrcene are comprised almost entirely of frequencies of either isoprene or trimethylethylene.

If a rubber molecule consists of long chains of the structural unit with an isoprene group at the end of the chain,[13] we might expect the Raman spectrum to show the double bond line as a doublet similar to that for myrcene but with the 1640 cm.$^{-1}$ component of a small relative intensity depending upon the length of the chains. The fact that the 1640 cm.$^{-1}$ line does not appear may be taken as evidence that the chains are so long that the isoprene group cannot be detected by this method. Our experiments indicate that 5% of isoprene can be detected in trimethylethylene but 1% cannot be.

Although the double bond frequency for balata is the same as that for rubber, the spectra of the two materials appear to be somewhat different. In general, *cis* and *trans* compounds show differences in their Raman spectra[5] (p. 239), so that the evidence can be looked upon as supporting this relationship between rubber and balata.

We hope to secure a Raman spectrum for vulcanized rubber, using diffusion rubber vulcanized by the Peachey process, and also to study some other rubber derivatives by this method. Results here would open a field of study in which very little indeed is known of the primary chemical linkages.

Abstract

A Raman line spectrum has been secured for rubber and balata by using clear gels of the purified hydrocarbons. It was not found possible to eliminate the background entirely. The most intense frequency for both rubber and balata is the same, 1670 cm.$^{-1}$, ascribed to the double bond.

Comparison of the frequencies for rubber and balata with those of trimethylethylene, myrcene, isoprene and limonene shows that the primary linkages in rubber are very similar to those in trimethylethylene, thus supporting the view that the rubber molecule consists of a long chain of isopentene units. Differences in the spectra require an explanation, however. The spectrum of balata shows differences from that of rubber such as might be expected from a *cis–trans* relationship.

The spectrum of myrcene is largely a superposition of the isoprene and trimethylethylene spectra.

Akron, Ohio Received October 22, 1935

---

[13] Memmler, "Science of Rubber," Am. Ed. Reinhold Publishing Corp., New York City, 1934, p. 236.