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Raman Spectra of Some Disubstituted Diacetylenes*

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Raman frequencies and relative intensities are reported for dimethyldiacetylene, diethyldiacetylene, dipropyldiacetylene, dibutyldiacetylene, and diamyldiacetylene. Depolarization factors also were obtained except for diethyldiacetylene. The relative intensities and depolarization factors were obtained with the use of a Gaertner microdensitometer. A tentative assignment was made of all the observed Raman frequencies of dimethyldiacetylene, assuming that it has the symmetry D'_{3h}. Using the chain and methyl group frequencies thus established for dimethyldiacetylene, a comparison was made with the other spectra in order to determine how these frequencies are affected by introducing additional CH_2 groups into the dimethyldiacetylene molecule. A comparison was made of the Raman spectra of the disubstituted diacetylenes with those of the corresponding acetylenes. For dimethyldiacetylene, three cases of Fermi resonance occurred, but there were also two cases where only a single line was observed, in spite of the fact that the frequency and symmetry conditions for resonance were satisfied. The carbon-carbon triple-bond frequency, which appears at 2183 cm^{-1} for diacetylene, increases to 2264 for dimethyldiacetylene, then drops to 2251–2257 for the other four compounds.

INTRODUCTION

PREVIOUS investigations in this laboratory and elsewhere have shown that disubstituted acetylenes generally have two or more lines near 2200 cm^{-1}. It seemed worth while to extend these investigations to see if the same behavior is exhibited by the disubstituted diacetylenes. Moreover, diacetylene itself has a very strong line at 2183 cm^{-1} which has been identified by Timm and Mecke[1] with the totally symmetrical frequency involving the carbon-carbon triple bond.

If each of the hydrogen atoms of diacetylene is replaced with the same alkyl radical, one would expect this change to affect the above-mentioned frequency. Also since the Raman spectra of the corresponding disubstituted acetylenes have been obtained, a comparison of the spectra of the disubstituted acetylenes and diacetylenes should reveal information about the frequencies which may have a similar origin in the two types of compounds. The molecules selected were dimethyldiacetylene (2,4-hexadiyne), diethyldiacetylene (3,5-octadiyne), dipropyldiacetylene (4,6-decadiyne), dibutyldiacetylene (5,7-dodecadiyne), and diamyldiacetylene (6,8-tetradecadiyne). All of these compounds have the characteristic diacetylenic structure, $R-C\equiv C-C\equiv C-R$. No previous Raman or infra-red data could be found for any of the five compounds.

[1] B. Timm and R. Mecke, Zeits. f. Physik **94**, 1 (1935).

TABLE I. Comparison of the Raman spectra of the disubstituted diacetylenes with the spectra of the corresponding acetylenes.*

Dimethyl-acetylene			Dimethyl-diacetylene			Diethyl-acetylene			Diethyl-diacetylene			Dipropyl-acetylene			Dipropyl-diacetylene			Dibutyl-acetylene			Dibutyl-diacetylene			Diamyl-acetylene			Diamyl-diacetylene		
Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ	Δν	I	ρ
									150	vw																			
												(165)	(2b)					169	1b	0.8									
213	VW					±206	6vb	0.8																					
			±247	80	0.64																								
												342	1																
371	VVS	D				±364	3vb	0.7				±371	5	0.9				371/389	3/3	0.6				373	3	0.9			
																								383	1				
																		416	2	0.8									
																								435	1				
															458	29													
												468	2b	0.7							±467	45	0.86				468	38	0.48
			±475	220	0.64																								
									479	10					±480	44	0.70												
						484	1														±484	31	0.79						
																								487	15	0.75			
						499	3	0.7																					
												(509)	(0)																
									521	4																			
															526	6													
						532	2					534	0																
																					540	4		539	4	0.86			
																		547	1b	0.7									
												551	1																
												578	1											(580)	vw				
																					(672)	vw							
												674	2	0.9										(675)	vw				
			(686)	vw		681	2																						
693	M	P				695	2																						
774	M	P				782	3	p	778	vw																			
																		803	3	0.7	803	6							
												808	3	0.4				811	4	0.4									
																								827	4				
															846	7	0.24							842	2	0.6			
												855	4	0.5															
																					866	vw							
																		873	3	0.6									
															882	10	0.16							887	1	0.8			
												891	5	0.5				901	3	0.6									
						918	2																						
																		929	2	0.7									
			(957)	vw					953	3											956	vw					(956)	vw	
																		960	2	0.7									
																								970	1	0.9			
						983	7	0.3													(993)	vw							
1029	M	D	1020	vw								1020	1	0.9										1024	1	0.9			
												1037	2		1037	3		1049	4	0.7	1048	7	0.27						
						1064	8	0.3	1063	5		1069	1	0.9										1067	3	0.8	1063	4	
												1095	4	0.5	1091	11	0.40				1101	11	0.64	1110	4	0.8	1104	10	0.19
																		1104	5	0.7									
																		1141	1										
			(1151)	vw																									
			(1185)	vw																									
						1207	½											1204	1										
																								1221	1		1219	8	0.40
			(1228)	vw					1231	6		1227	2	0.6	1228	10	0.47	1235	2	<0.7	1228	12	0.29						
			1253	17		1259	2	0.9	1254	vw		1260	3	0.6	1256	7	0.41												
												1274	1											1271	1				
												1291	1		1293	3		1295	3	0.8	1291	5	0.31	1300	3	0.9	1297	5	
						1319	7	0.6	1330	7		1327	5	0.6	1329	12	0.57	1326	4	0.6	1329	17		1330	3	0.9	1329	12	0.37
												1350	2	p	1347	9	0.61				1348	vw							
1380	S	P	1381	115	0.62	1376	2	p	1375	1																			
			1426	5											1425	15	0.83				1423	21	0.56	1436	6	0.8	1425	18	0.39
						1439	5	0.7	1430	8		1434	5	0.8															
1448	MS	D	1458	vw		1460	4	0.8	1461	5		1456	4b	0.8	1452	10	0.55	1440/1457	5/3b	0.8	1443	17	0.47	1452	3	0.8	1450	11	0.49
						2200	1	p										2195	0										
			2225	vw																									
2233	VS	P	2264	1000	0.40	2231	9	0.4	2257	1000		2234	10	0.5	2256	1000	0.33	2233	8	0.4	2251	1000	0.47	2231	7	0.4	2255	1000	0.19
						2247	8	0.4										2245	2	0.4				2248	2				
												2292	6	0.5				2296	5	0.4				2294	4	0.4			
2310	VS	P	2309	9		2301	6	0.4																						
			2502																											
2737	MW					2729	2	p				2736	2	p				2729	1b	<0.9									
			2821	vw		2850	5	0.2	2836	12		2841	5	0.4	2830	10	0.22	2841	4	0.2	2827	13		2852	6		2827	vw	
2857	M		2848	21		2883	4	0.3	2884	28		2871	8	0.2	2869	48	0.26	2865	7		2864	58	0.16	2874	6	0.3	2861	44	0.20
2916	VS	P	2914	400	0.17	2909	10b	0.3	2913	59		2905	9	0.5	2904	81	0.35	2909	10	0.6	2902	110	0.30	2906	10	(0.6)	2900	93	0.27
						2939	10	0.1	2939	47		2936	9	0.4	2932	62	0.41	2931	8	0.1	2926	77	0.47	2934	8	0.1	2922	46	0.29
2966	MW		2954	39		2978	7	0.7	2982	25		2971	6	0.9	2966	21		2967	5	0.8	2957	23	0.69	2957	4	0.9	2956	vw	

* Δν=Raman displacement in cm⁻¹, I=estimated relative intensity if intensity of strongest line is 10, but if intensity of strongest line is 1000 then I is the relative intensity measured with the densitometer, b=broad, vb=very broad, S=strong, VS=very strong, M=medium, MS=medium-strong, W=weak, MW=medium-weak, VW=very weak, vw=lines that were too weak to measure with the microdensitometer, ρ=depolarization factor ±indicates observation both as Stokes and anti-Stokes lines, parentheses enclose data in regard to which there is some question, D=depolarized (ρ=6/7), P=polarized (ρ≤6/7), p means ρ was less than 6/7 but that it was not possible to make a quantitative measurement, and the brace joins lines that were unresolved on the polarization spectrogram. Data for dimethylacetylene were obtained from B. L. Crawford, Jr., J. Chem. Phys. 7, 555 (1939); for diethylacetylene and dipropylacetylene from Forrest F. Cleveland, M. J. Murray, and H. J. Taufen, J. Chem. Phys. 10, 172 (1942); for dibutylacetylene from M. J. Murray and Forrest F. Cleveland, J. Am. Chem. Soc. 63, 1718 (1941), and for diamylacetylene from Forrest F. Cleveland and M. J. Murray, J. Am. Chem. Soc. 62, 3185 (1940).

EXPERIMENTAL

Using the technique and apparatus described in previous papers,[2] spectrograms were obtained which were used to determine Raman frequencies, relative intensities, and depolarization factors. It was necessary to obtain some of the spectrograms with a fast Hilger E-518 spectrograph on account of the rapid decomposition of one of the samples. All of the samples were in the

[2] Forrest F. Cleveland, M. J. Murray, J. R. Coley, and V. I. Komarewsky, J. Chem. Phys. 10, 18 (1942); Forrest F. Cleveland, J. Chem. Phys. 11, 1 (1943).

TABLE II. A tentative assignment of the Raman frequencies of dimethyldiacetylene.*

Diacetylene			Dimethyldiacetylene				Dimethylacetylene			
Designation	$\Delta\nu$	Type of vibration	$\Delta\nu$	I	ρ	Assignment and symmetry	$\Delta\nu$	I	ρ	Assignment and symmetry
ν_9	230	deformation	247	80	0.64	Fund. E or $\bar{E}$				
ν_8	488	deformation	475	220	0.64	Fund. $\bar{E}$				
ν_3	644	C−C stretching	(686)	vw		Fund. A_1				
ν_1	(3350)	C−H stretching	(957)	vw		Fund. A_1				
			1020	vw		Fund. $\bar{E}$	1029	M D		Fund. $\bar{E}$
			(1151)	vw		$686+475=1161,\ \bar{E}$				
			(1185)	vw		$1442-247=1195,\ \bar{A}_1+\bar{A}_2+\bar{E}$ or A_1+A_2+E				
			(1228)	vw		$957+247=1204,\ E$ or $\bar{E}$				
			1253	17		$1020+247=1267,\ \bar{A}_1+\bar{A}_2+\bar{E}$ or A_1+A_2+E				
			1381	115	0.62	Fund. A_1	1380	S P		Fund. A_1
			1426	5		$\left.\begin{array}{l}\text{Fund. } 1442,\ \bar{E}\\ 957+475=1432,\ \bar{E}\end{array}\right\}$	1448	MS D		Fund. $\bar{E}$
			1458	vw						
			2225	vw		C^{13} isotope				
ν_2	2183	C≡C stretching	2264	1000	0.40	$\left.\begin{array}{l}\text{Fund. } A_1\\ 957+1381=2338,\ A_1\end{array}\right\}$				
			2309	9						
			2502	vw		$2264+247=2511,\ E$ or $\bar{E}$				
			2821	vw		$\left.\begin{array}{l}1381^2=2762,\ A_1\\ 1442^2=2884,\ A_1+E\\ \text{Fund. } A_1\end{array}\right\}$	2737	MW		$1380^2=2760,\ A_1$
			2848	21			2857	M		$1448^2=2896,\ A_1+E$
			2914	400	0.17		2916	VS P		Fund. A_1
			2954	39		Fund. $\bar{E}$	2966	MW		Fund. $\bar{E}$

* All symbols have the same meaning as in Table I with the exception of the braces which indicate probable cases of Fermi resonance.

liquid state with the exception of dimethyldiacetylene which was put into solution in CCl_4. Excitation was by Hg 4358A. The intensities and depolarization factors were determined by use of a Gaertner microdensitometer as described elsewhere.[3] No polarization spectrogram could be obtained for diethyldiacetylene.

An outline of the method of preparation of the compounds is as follows:

Dimethyldiacetylene, C_6H_6: About 500 cm³ of liquid ammonia were placed in a 2-l, three-necked flask and 25 g of sodium were added in small pieces as acetylene was bubbled through the ammonia until the blue color of the solution disappeared.[4] The acetylene had been washed by passing through two bottles containing H_2SO_4 and then had been dried by passing over soda lime. A dry-ice acetone condenser was used.

After adding dropwise 130 g of $(CH_3)_2SO_4$, the mixture was allowed to stand $\frac{1}{2}$ hr. Water was then added continuously and the gases evolved were passed through freshly prepared ammoniacal Cu_2Cl_2. When no more gas was evolved as water

was added, the precipitated acetylide was filtered off using suction and washed until free of the blue color in the filtrate. It was then suspended along with the filter paper in 500 cm³ of water and 110 g of $K_3Fe(CN)_6$ were added.[5] The resulting mixture was steam distilled until no more product was obtained. The water was poured off the resulting white solid, $CH_3-C\equiv C-C\equiv C-CH_3$, which was then dissolved in CCl_4 and dried with Drierite. The solution was placed in a distilling flask and both CCl_4 and dimethyldiacetylene were distilled into the Raman tube in a partial vacuum.

The other compounds were prepared by the following method: The monosubstituted acetylene was obtained from acetylene, sodium, liquid ammonia, and the bromide of the radical being substituted for the hydrogen of the acetylene. The acetylenic Grignard reagent was formed in dry ether, using ethylmagnesium bromide. Using an ice bath, $CuBr_2$ was added slowly and with vigorous stirring to the acetylenic Grignard reagent.[6] When the reaction was complete, ice was added and the disubstituted diacetylene was

[3] Forrest F. Cleveland and M. J. Murray, J. Chem. Phys. 11, 450 (1943).
[4] Cf. T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, J. Org. Chem. 2, 1 (1937).

[5] Cf. G. Griner, Ann. Chim. Phys. [6] 26, 354 (1892).
[6] James P. Danehy and J. A. Nieuwland, J. Am. Chem. Soc. 58, 1609 (1936).

then separated from the pasty mass by steam distillation. The boiling points of the compounds thus prepared were as follows:

Diethyldiacetylene, C_8H_{10},	77.5–80.0°C at 34 mm Hg,
Dipropyldiacetylene, $C_{10}H_{14}$,	76.0°C at 2 mm Hg,
Dibutyldiacetylene, $C_{12}H_{18}$,	97.0°C at 3 mm Hg,
Diamyldiacetylene, $C_{14}H_{22}$,	121.4°C at 2 mm Hg.

RESULTS

The experimental results for the disubstituted diacetylenes are listed in Table I. Also in Table I are given, for comparison purposes, the corresponding data for the disubstituted acetylenes, as reported by various observers. All the samples seemed to be fairly pure since no recognizable impurity lines were found in the Raman spectra, with the exception of diethyldiacetylene for which a very weak line was observed at 2179 cm⁻¹. This might indicate the presence of a trace of diacetylene as an impurity since diacetylene has its strongest line at 2183 cm⁻¹.

DISCUSSION

Probably the most outstanding characteristic of the Raman spectra of these disubstituted diacetylenes is the very strong line which appears for each compound in the 2250–2265 cm⁻¹ region. Comparison with other molecules containing the acetylenic linkage indicates that this line is associated with the carbon-carbon triple-bond frequency. For diacetylene a similar line occurs at 2183 cm⁻¹. From Table I it appears that the greatest change in this frequency is produced when the two hydrogen atoms of diacetylene are replaced with methyl groups as this frequency has a greater value for dimethyldiacetylene than for any of the other diacetylenes investigated. Addition of CH_2 groups to the methyl groups which replace the hydrogen atoms does not seem to produce a greater shift, but results in a slight lowering of the Raman frequency, as observed for the other disubstituted diacetylenes. Furthermore, in all the disubstituted diacetylenes studied, with the exception of dimethyldiacetylene, only one line was observed in the 2200–2300 cm⁻¹ region. This is somewhat different from the disubstituted acetylenes which usually have two or more lines in the same region.

Assuming that dimethyldiacetylene has the same symmetry as dimethylacetylene D'_{3h}, the

tentative assignment of the Raman frequencies shown in Table II was made. The chain frequencies were established by comparison with Wu and Shen's[7] analysis of the vibrational spectrum of diacetylene. Crawford's[8] analysis of the dimethylacetylene Raman spectrum was used in determining the methyl group frequencies.

As a further aid in the analysis, the selection rules for fundamentals, binary combinations, overtones of non-degenerate frequencies, overtones of doubly degenerate frequencies up to the fourth overtone, for a molecule whose symmetry is D'_{3h}, and the number of frequencies of each type for dimethyldiacetylene, were obtained by methods described elsewhere.[9] The selection rules will not be listed here since they have already been published in a condensed form.[10] The selection rules allow five fundamental frequencies of type A_1, five of type E, and five of type $\bar{E}$ to appear in the Raman spectrum and four type $\bar{A}_2$ and the five E fundamentals to appear in the infra-red spectrum. The A_1 fundamentals should be polarized and the E and $\bar{E}$ frequencies should be depolarized. Unfortunately, no infra-red data were available and the tentative assignments therefore had to be based upon the Raman data alone. It is quite possible that these assignments may require revision if and when the infra-red data become available.

Without the calculated values of the fundamental frequencies it was not possible to give a unique assignment of the 247, 1185, 1228, 1253, and 2502 lines, since for these two assignments are possible depending upon whether the 247 fundamental is E or $\bar{E}$. However, it was possible to decide that the 475 cm⁻¹ line was an $\bar{E}$ fundamental frequency in the following way: In order to have Fermi resonance between the $1442\bar{E}$ fundamental and the 1432 combination frequency, the symmetry condition requires[9] that the 1432 frequency have $\bar{E}$ symmetry. Since, according to the present assignment, 1432 cm⁻¹ results from the combination of the $957A_1$ funda-

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[7] T. Y. Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (National University of Peking, Kunming, China, 1939), page 259.

[8] B. L. Crawford, Jr., J. Chem. Phys. 7, 555 (1939).

[9] Arnold G. Meister, Forrest F. Cleveland, and M. J. Murray, Am. J. Phys. 11, 239 (1943).

[10] Reference 7, page 296.

mental and the 475 fundamental, the 475 fundamental would have to be of $\bar{E}$ symmetry so that the combination frequency would have $\bar{E}$ symmetry. This is true because from the selection rules one sees that a combination of an A_1 frequency with an $\bar{E}$ frequency will have the symmetry $\bar{E}$.

Besides the case mentioned above, two other cases of Fermi resonance appear as shown in Table II. The first occurs between the $2264A_1$ fundamental and the 2309 combination frequency which results, according to the present assignment, from the combination of the 957 and $1381A_1$ fundamental frequencies. The other case appears to be more complicated, for now three frequencies seem to be interacting with one another; they are the first overtone of the $1381A_1$ fundamental, the first overtone of the $1442\bar{E}$ fundamental, and the $2914A_1$ fundamental.

Two other cases of Fermi resonance appear to be possible but were not observed. For example, the first overtone of the $475\bar{E}$ fundamental frequency would have the proper symmetry and energy level value to interact with the $957A_1$ fundamental. Yet in spite of this possibility no other line was observed in this region. However, the 957 cm^{-1} fundamental was quite weak and it is possible that the resonance component might have escaped observation. Another possible case of resonance which was not observed could occur between the first overtone of the $686A_1$ fundamental and the $1381A_1$ fundamental, since both the overtone and the fundamental frequency would have the same symmetry, A_1, and $686^2 = 1372$.

If one assigns the line at 1185 cm^{-1} to the difference tone $(1442-247)$, one would expect a line to appear at $(1442+247) = 1689$ cm^{-1}, for according to Herzberg,[11] if a difference tone is present, the corresponding summation frequency, since it is undiminished by a Boltzmann factor, should appear with even greater intensity. Also, for the same reason, if the line at 2225 cm^{-1} is assigned to the $(2914-686)$ difference tone, one would expect a line to be found at $(2914+686) = 3600$ cm^{-1}. Yet in neither of these cases were lines observed in the Raman spectrum. In view

of this difficulty, it seems better to assign the 2225 cm^{-1} line to the triple-bond frequency of an isotopic molecule containing C^{13}. Another alternative might be that dimethylacetylene was present as an impurity. Since this compound has very strong lines at 2233 and 2310 cm^{-1}, the lines at 2225 and 2309 cm^{-1} could indicate the presence of a trace of dimethylacetylene, although this seems improbable in view of the method of preparation.

A study of Table II indicates that of the fifteen fundamental frequencies which are permitted in the Raman effect, only ten have been given an assignment. All five A_1 fundamental frequencies seem to have been observed, but only four or possibly five of the $\bar{E}$ fundamental frequencies were observed, depending on the final assignment of the 247 cm^{-1} line which tentatively has been assigned to an E or $\bar{E}$ fundamental. For the same reason only one or none of the five E frequencies was observed. This same scarcity of E fundamentals was observed by Crawford[8] in his analysis of the Raman spectrum of dimethylacetylene; of the four E-type fundamental frequencies which were allowed in the Raman spectrum, only one was observed. Since for this compound all of the missing E fundamentals were observed in the infra-red spectrum, one would expect that if the infra-red spectrum of dimethyldiacetylene were obtained, it would help to determine the missing E-type fundamental frequencies. Of course, it is possible that some of the frequencies did not occur in the Raman spectrum because they lie too close to other frequencies and were thus not resolved, or else because the lines while they are permitted by the selection rules were too weak to be observed.

From Table I, it is possible to get a good indication of the behavior of the chain frequencies as CH$_2$ groups are added to the dimethyldiacetylene molecule. The 247 cm^{-1} E or $\bar{E}$ fundamental of dimethyldiacetylene either was not observed for the other disubstituted diacetylenes or else its value was changed considerably, as the other compounds have no line near this value. On the other hand, the 475 cm^{-1} $\bar{E}$ fundamental frequency seemed to increase slightly as more CH$_2$ groups were added, each compound having a line in the 475–490 cm^{-1} region with diamyl-

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[11] G. Herzberg, private communication.

diacetylene having the greatest frequency value. In contrast to this behavior the $686A_1$ fundamental frequency seemed to decrease slightly, but whether the decrease is significant is hard to say since this frequency was not observed in the spectra of two of the disubstituted diacetylenes. The 957 cm^{-1} A_1 fundamental was observed in only three of the other compounds and was not very strong in any of the four cases. Finally, the 2264 cm^{-1} A_1 fundamental appears to be affected very little since its value for the other four compounds lies between 2251–2257 cm^{-1}.

In a similar manner one can observe the behavior of the methyl group frequencies. The 1020 cm^{-1} $\bar{E}$ fundamental seems to be changed considerably or else was not observed in some cases since only two compounds had lines which were found near this value. A similar behavior is shown by the 1381 cm^{-1} A_1 fundamental since diethyldiacetylene was the only compound which had a line near this value. The 1442 cm^{-1} $\bar{E}$ frequency seems to be present in all the compounds, although its value seems to change rather sporadically from one compound to another. A similar behavior is exhibited by the 2914 cm^{-1} A_1 fundamental since it is found for all the compounds in the 2922–2939 cm^{-1} region. The line lying in this region has been chosen as corresponding to the A_1 fundamental rather than the line which appears for all the compounds in the 2900–2913 region, because if one compares the ratio of the intensity of the line in the 2900–2913 region to the intensity of the line in the 2922–2939 region, one finds that the ratio increases as the number of CH$_2$ groups increases, having its greatest value for diamyldiacetylene. So the line in the 2900–2913 cm^{-1} region is believed to be

associated with the CH$_2$ groups while the line in the 2922–2939 cm^{-1} region is associated with the methyl group. Furthermore, it has been shown[12] that the methyl group usually has a polarized frequency in the 2930 cm^{-1} region, so it seems more reasonable to associate the line in this region with the polarized frequency of the methyl group. All that remains is the 2954 cm^{-1} $\bar{E}$ fundamental frequency which seems to be present in all of the compounds; its value changes considerably from compound to compound at first but for the last two compounds in the table is about the same. This frequency has its greatest value for diethyldiacetylene.

ACKNOWLEDGMENTS

[12] Forrest F. Cleveland, M. J. Murray, H. H. Haney, and Julia Schakelford, J. Chem. Phys. 8, 153 (1940); Forrest F. Cleveland and M. J. Murray, J. Am. Chem. Soc. 62, 3185 (1940).