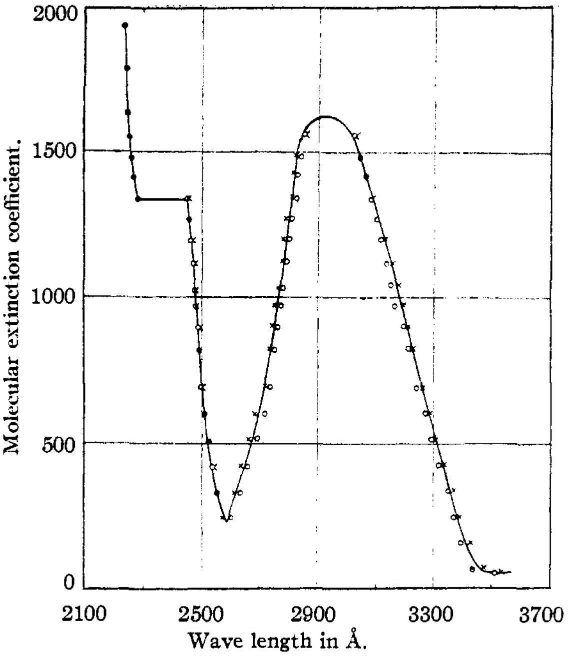

Fig. 2.—Absorption curve of rotenone in ethyl alcohol solution. The plotted curve is for the solution measured immediately after preparation and not saturated with either oxygen or carbon dioxide; the observed values for similar solutions kept in the darkroom for twenty days and saturated with these gases are also indicated: (O) saturated with oxygen, (×) saturated with carbon dioxide.

ethyl alcohol solution. Jones[1] found that, of the various organic solvents studied, rotenone in pyridine solution changed color most rapidly, while in the case of alcohol and benzene solutions the change is almost imperceptible. This suggests that the oxidation, if occurring, depends to a large extent upon the nature of the solvent used. It would be interesting to study how pyridine differs from alcohol in influencing this decomposition of rotenone, but the fact that pyridine and rotenone both show high absorption in about the same region of the spectrum makes such a study impossible.

On the other hand, the effect of light on the decomposition of rotenone is very marked. It should be noted that the absorption spectra for both of the exposed solutions, that is, the solutions saturated with carbon dioxide and with oxygen (Fig. 1), gradually changed in shape as the period of exposure increased, until the absorption maximum finally disappeared altogether. It is apparent from the curves that for the same period of exposure the absorption spectra of carbon dioxide and oxygen treated solutions differ only slightly. This slight difference could mean only that the effect of oxygen in the photo-decomposition of rotenone is at least very small.

Summary

Study of the absorption spectra of solutions of rotenone in ethyl alcohol, saturated with carbon dioxide and with oxygen, exposed and unexposed to sunlight, showed that oxygen does not decompose rotenone in the dark. In light, however, there is marked decomposition, an effect which does not seem to be due appreciably to the presence of oxygen.

Peiping, China Received November 12, 1940

[Contribution from the Departments of Chemistry and Physics, Illinois Institute of Technology]

Raman Spectra of Acetylenes. V. Alkyl Acetylenes

By M. J. Murray and Forrest F. Cleveland

The main purpose of this series of papers[1] has been to determine what changes occur in the 2200 cm.$^{-1}$ region of the Raman spectra of acetylenic compounds when various groups are adjacent to the triple bond carbon and thus to obtain additional information in regard to the occurrence of more lines in this region for disubstituted than for monosubstituted acetylenes. The considerations given in paper IV indicate that some of the additional weak lines are due to isotopic molecules containing a carbon atom of mass thirteen, as was suggested for dimethylacetylene by Glockler and Renfrew[2] and by Crawford.[3]

An interesting observation[4] has been made in the case of 6-dodecyne. When this compound was allowed to stand in contact with air, an oxygen atom replaced the two hydrogen atoms on one of the carbon atoms adjacent to the triple bond carbon. The resultant 6-dodecynone-5 had only a single line at 2212 (10), whereas the parent 6-

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(1) I, This Journal, **60**, 2664 (1938); II, *ibid.*, **61**, 3546 (1939); III, *ibid.*, **62**, 3185 (1940); IV, *J. Chem. Phys.*, **9**, 390 (1941.)

(2) G. Glockler and M. M. Renfrew, *ibid.*, **6**, 340 (1938); *ibid.*, **6**, 408 (1938).

(3) B. L. Crawford, Jr., *ibid.*, **7**, 555 (1939).

(4) M. J. Murray and Forrest F. Cleveland, This Journal, **63**, 1363 (1941).

dodecyne had three lines at 2231 (7), 2248 (2) and 2294 (4). Apparently the oxygen atom had lowered the triple bond frequency so that it was no longer in sufficiently exact coincidence with the overtone frequency (or frequencies) to produce any observable resonance splitting. Or perhaps the removal of the hydrogen atoms from the carbon atom removes or changes one or both of the lower fundamentals involved in the resonance interaction. The fact that only one line has been observed for other disubstituted acetylenes which have no hydrogen atoms on this carbon appears to substantiate the latter view,[1,5] although in one case[1] a closely spaced doublet was observed.

The present paper is a report of the Raman spectra of the alkyl acetylenes, 1-heptyne, 4-methoxy-1-butyne, 2-octyne, 3-octyne, 5-decyne, 7-tetradecyne, and 9-octadecyne.

Experimental

The acetylenes were supplied by Dr. G. F. Hennion of the University of Notre Dame and were prepared according to procedures previously described.[6] The authors are grateful for this assistance.

The apparatus and experimental technique were essentially the same as described in paper II. The liquid samples used in obtaining the spectra were purified immediately before exposure by distillation in a 30-cm., Podbielniak type, heated column. This was necessary since experience indicated[4] that many acetylenes upon standing become contaminated by reaction with atmospheric oxygen to form ketones. The boiling points of the compounds are as follows: 1-heptyne, 98.4–98.6°; 4-methoxy-1-butyne, 87.4–88.0°; 2-octyne, 135.5–137.5°; 3-octyne, 132.5–132.8°; 5-decyne, 75° (23 mm.); 7-tetradecyne, 101° (3 mm.); 9-octadecyne, 163–164° (7 mm.). The slit width for the regular exposures was 0.08 mm. and 0.12 mm. for the polarization exposures.

Results

The results obtained for the seven compounds are listed in Table I. The presence of strong continuous background on spectrograms of 9-octadecyne made impossible the measurement of depolarization factors and lines of low intensity for this compound.

Discussion

Previous Data.—Results were found in the literature only for 1-heptyne[7,8] and 2-octyne.[8,5]

Raman displacements which correspond to those previously observed for these compounds are set in **bold type** in Table I. In general, the agreement is quite good. For 1-heptyne, however, the strong line listed by Magat[9] as 2940 was observed in the present study at 2925. For 2-octyne, the line previously reported at 280 was resolved into the doublet 263, 296. On the other hand, the doublet 963, 978 listed by Magat appeared as the single line 972. Also for the latter compound, the line previously reported as 2920(5) was found to be the doublet 2916(6), 2939(10). The infra-red absorption spectrum of 1-heptyne has been obtained by Lambert and Lecomte.[10]

Frequencies below 2000 cm.$^{-1}$.—The displacements near 200 cm.$^{-1}$ probably correspond to deformation vibrations. They are more intense in the two monosubstituted acetylenes than in the five disubstituted acetylenes. This is in agreement with the results reported for other compounds in paper III. The strong frequency near 375 in the disubstituted acetylenes has a value near 335 in the monosubstituted acetylenes. This agrees with Grédy's findings for a considerable number of acetylenes. As she observed, the 335 frequency disappears or is considerably weakened when the carbon adjacent to the triple bond is tertiary. The fact that this frequency is strong for the two monosubstituted acetylenes in the present paper and weak or absent for the five in paper III adds weight to this conclusion. Crawford[3,11] ascribes the corresponding frequencies in methyl and dimethylacetylene to bending of the $C\equiv C—CH_3$ angle. The two monosubstituted acetylenes also have a frequency near 630 cm.$^{-1}$ which was not observed for the five disubstituted compounds. Following Crawford, this may be attributed to the deformation frequency involving the $C\equiv C—H$ angle. All seven compounds have a frequency near 815 cm.$^{-1}$ which is considerably polarized.

Frequencies near 1040, 1075, 1115, 1300, 1440 and 1460 are observed quite generally for compounds having hydrocarbon groups. The ones at 1075, 1300 and 1460 may be attributed to chain frequencies.[12] Comparison with Crawford's results for methyl and dimethylacetylene indicates that the 1040 and 1440 frequencies, as

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[5] Blanche Grédy, *Compt. rend.*, **196**, 1119 (1933); **197**, 327 (1933); **198**, 89, 2254 (1934); **199**, 294, 1129 (1934); Thèses, Paris, 1935.

[6] Hennion, *et al.*, *J. Org. Chem.*, **2**, 1 (1937); THIS JOURNAL, **59**, 1310 (1937); **60**, 1717 (1938); *Proc. Indiana Acad. Sci.*, **47**, 116 (1938).

[7] R. Courtel, *Diplôme d'études supérieures*, Paris, 1932.

[8] M. M. Bourguel and P. Daure, *Compt. rend.*, **190**, 1298 (1930); *Bull. soc. chim.*, **47**, 1349 (1930).

[9] M. Magat, "Tables annuelles de constants et données numériques," Volume XI, Gauthier-Villars, Paris, 1936.

[10] P. Lambert and J. Lecomte, *Ann. phys.*, **10**, 503 (1938).

[11] B. L. Crawford, Jr., *J. Chem. Phys.*, **8**, 526 (1940).

[12] *Cf.* S. E. Whitcomb, H. H. Nielsen and L. H. Thomas, *ibid.*, **8**, 143 (1940).

TABLE I[a]

RAMAN SPECTRA OF THE ALKYL ACETYLENES

1-Heptyne			4-Methoxy-1-butyne			2-Octyne			3-Octyne			5-Decyne			7-Tetradecyne			9-Octadecyne	
$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I	ρ	$\Delta\nu$	I
178	3b	0.7	±150	4b	0.7							169	1b	0.8					
212	3b		205	3b	0.7	211	3												
						263	1												
309	2	0.7				296	1												
336	5		±338	6	0.7														
353	3					**349**	2												
						±**375**	7	0.7	376	2	0.7	371	3	0.6	372	4	0.7	364	2
												389	3						
434	1		418	3	0.6	**438**	1					416	2	0.8	[434	1	0.9]		
						460	1		464	1		474	1b	0.7					
507	1		508	1	0.9	**515**	1		494	1b									
548	1		570	1	0.9	**539**	2		556	1b		547	1b	0.7					
						567	1												
626	3b	0.9	627	2b	0.7														
			659	2b		685	1		677	1									
763	1								781	1					771	1			
826	3	0.4	822	4	0.5	**803**	1		800	2	P	803	3	0.7					
									812	2		811	4	0.4	810	1			
849	1		846	1	P	**841**	3	P							864	2	P		
						889	1		874	2		873	3	0.6	889	3	P		
									897	2		901	3	0.6					
944	1		924	1					945	1		929	2	0.7					
962	1											960	2	0.7					
974	1		980	3	0.4	**972**	1		970	1					996	2	0.6		
1004	1		1017	1											1013	2			
1035	2	P	1047	2	0.7	1029	1		1050	3	0.6	1049	4	0.7	1051	1			
1077	3	0.7	1061	1	0.9	**1064**	2	0.7	1064	4					1074	3b	0.6	1075	2
1111	4	0.7	1116	3	0.7	**1110**	3	0.9	1103	4	0.6	1104	5	0.7	1112	5	0.4	1115	3
			1155	1		1150	1					1141	1						
												1204	1						
			1276	3b	0.8	1273	1					1235	2	<0.7					
1305	4	0.7				**1305**	3	0.7	1299	2		1295	3	0.8	1305	4	0.7	1294	3
1336	3		1335	3	0.8	**1335**	3	0.7	1324	5	0.6	1326	4	0.6	1329	3	0.7		
			1382	2	0.8	**1382**	6	0.7											
			1422	2	0.7														
1444	5b	0.8	1438	5		**1444**	6	0.9	1440	6	0.7	1440	5	0.8	1439	7	0.7	1438	6
1458	3b		1454	3		**1460**	3		1457	3b		1457	3b		1457	4b	0.7	1454	3
			1482	2	0.7														
2064	0		2064	0															
2097	0		2094	0															
2118	10	0.4	2118	10	0.2														
						2198	0		2199	0		2195	0						
						2233	10	0.4	2235	8	0.4	2233	8	0.4	2233	7	0.4	2231	7
						2256	1		2249	1		2245	2	0.4	2252	2	0.4		
						2305	8	0.4	2296	6	0.4	2296	5	0.4	2294	5	0.4	2290	4
2723	1		2740	1	<0.7	2731	1		2730	2	<0.4	2729	1b	<0.9	2732	1b			
			2828	6	0.1														
2861	6b	0.1	2863	3	[0.6]	**2854**	7	0.1	2851	6	0.1	2841	4	0.2	2854	8b	0.1	2859	8
2908	8b	0.3	2893	3		**2892**	5	0.7	2872	6		2865	7						
2925	8b	0.1	2918	8	0.1	**2916**	6		2907	10	0.6	2909	10	0.6	2903	10b	0.6	2905	10
			2939	3		2939	10	0.1	2927	8	0.1	2931	8	0.1	2927	9b	0.1	2931	8
2964	4	0.9	[2965	1]		**2961**	4	0.9	2974	6	0.9	2967	5	0.8	2963	4	0.9	2963	3
			2989	4	0.8														
3292	1		3296	1b	<0.9														
3309	2								Continuum										
medium			weak			weak			medium			medium			medium			strong	

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[a] $\Delta\nu$ Raman displacement in cm.$^{-1}$, I = estimated intensity, ρ = depolarization factor, b = unusually broad, ± means observed both as Stokes and anti-Stokes line, brace indicates lines that were unresolved on polarization spectrogram, P = polarized, brackets enclose data in regard to which there is some uncertainity, **bold type** indicates previously observed frequencies.

well as the 1382 frequency observed only for 4-methoxy-1-butyne and 2-octyne, are fundamentals of the CH_3 group. The first is a rocking frequency; the other two are CH bending vibrations. The intensity of the 1382 line in 2-octyne is remarkable in view of its absence in the spectrum of the similar molecules 3-octyne and all the other acetylenes except 4-methoxy-1-butyne. Apparently its intensity is greater when the methyl group is not adjacent to a $—CH_2—$ group. A fairly strong line near 1330 was observed for all except 9-octadecyne, for which the spectrum was incomplete.

Frequencies near 2000 cm.$^{-1}$.—As usual, the monosubstituted acetylenes gave only a single strong line at 2118 cm.$^{-1}$, although faint lines were observed at 2064 and 2097 for 1-heptyne and 2064 and 2094 for 4-methoxy-1-butyne. These may be attributed to the triple bond frequencies of the isotopic molecules, $R—C^{13}≡C^{12}—H$ and $R—C^{12}≡C^{13}—H$, respectively. Calculation from the valence force equations indicates that the values of the isotope shifts of these two isotopic forms for methylacetylene are -50 and -26 cm.$^{-1}$ (*cf.* paper IV), and it seems probable that the shifts for other monosubstituted acetylenes would be nearly the same. If this is the case, the frequencies expected for these molecules would be 2068 and 2092, respectively. It seems probable that the frequency observed at 2064 is an unresolved doublet composed of the isotopic frequency expected at 2068 and the triple bond frequency excited by Hg 4347 Å. which should fall at 2061 cm.$^{-1}$. Rough intensity measurements indicate that the intensities of the two lines should be approximately the same

The faint line observed near 2198 cm.$^{-1}$ in the spectra of the disubstituted acetylenes may be due to the isotopic molecule $R—C^{13}≡C^{12}—R'$ (*cf.* paper IV). Calculations from the valence force equations for dimethylacetylene indicate that the isotope shift should be -33.5 cm.$^{-1}$. The shift would probably be approximately the same for other disubstituted acetylenes.

If Fermi resonance interaction is to account for the remainder of the lines in this region in the spectra of dialkyl acetylenes, it seems probable that at least one fundamental in addition to the infrared active C—C≡C—C frequency (at 1126 in dimethylacetylene) must be involved. This may be an inner frequency (near 1100) of the $—CH_2—$ group, since a line at 2245 is observed in the Raman spectrum of diethylacetylene[13] (and in many other dialkylacetylenes, including the ones in the present paper) in addition to the two strong lines near 2230 and 2300 which constitute the well-known resonance doublet of dimethylacetylene.

Frequencies near 3000 cm.$^{-1}$.—The investigations described in the previous papers have shown that the Raman spectra of molecules containing CH_3 and $—CH_2—$ groups generally have strong, highly polarized frequencies near 2865 and 2930 and a weak, depolarized frequency near 2965 cm.$^{-1}$. Molecules with hydrocarbon chains have a frequency, somewhat polarized, near 2905. The present spectra also include these frequencies. In 2-octyne, the 2905 frequency was resolved into two components, while in 3-octyne and 5-decyne the 2865 frequency was resolved into two components. In 4-methoxy-1-butyne, the presence of the oxygen atom profoundly modifies the Raman spectrum in this region. The two strong, polarized lines for this molecule are at 2828 and 2918; while the weaker, depolarized frequency is at 2989 cm.$^{-1}$. The other four, still weaker, frequencies have approximately the same values as for the other molecules.

The frequency near 3300 is the one involving the acetylenic hydrogen. In 1-heptyne, it was resolved into two components. The lower component has the frequency to be expected for the isotopic molecule, $R—C^{12}≡C^{13}—H$ (calculations from the valence force equations indicate that the shift for dimethylacetylene would be -16 cm.$^{-1}$), but the intensity seems far greater than could possibly be expected from the relative abundance of the carbon isotopes.

Summary

Raman displacements, estimated intensities and depolarization factors are reported for 1-heptyne, 4-methoxy-1-butyne, 2-octyne, 3-octyne, 5-decyne, and 7-tetradecyne. Due to limitations imposed by the strong continuous background, only the frequencies and estimated intensities for the strongest lines of 9-octadecyne were obtained.

CHICAGO, ILLINOIS RECEIVED MARCH 21, 1941

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[13] H. Van Risseghem, *Bull. soc. chim. Belg.*, **47**, 271 (1938).