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THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC NITRATES

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Abstract

The infra-red absorption of four organic nitrates has been studied in the region from 1.0 to 7.5μ. The liquids used are methyl nitrate, ethyl nitrate, propyl nitrate and butyl nitrate. Two absorption bands at 1.40μ and 2.96μ are attributed either to an OH linkage or water. All other bands are attributed to the carbon-hydrogen linkage and as an additional CH_2 group is introduced, two characteristics appear, namely, the intensity of all bands decreases and a shift of from 0.01 to 0.06μ to longer wave-length occurs. No characteristic absorption spectra of the NO_3 group have been found to exist in the organic nitrates. Previous workers have found that the carbon-hydrogen linkage gives regions of intense absorption at about 3.43, 6.86, 8 to 10 and 12 to 18μ. In the present work an intense band was observed at 6.7μ but the observations were not carried past 7.5μ and the other two fundamental frequencies were not observed. However, from observed bands there has been calculated four regions of intense absorption, which are assumed to be the fundamental frequencies and all other bands observed are attributed to a combination or overtones of these fundamentals.

ORGANIC liquids which contain carbon and hydrogen have been found to have many similarities in their infra-red absorption bands and some success has been had in identifying the bands as due to certain groups of atoms within the molecule. A good idea of the energy changes which give rise to the absorption spectra has been obtained in methane from the experimental work of Cooley[1] and the theoretical work of Dennison.[2] Easley, Fenner and Spence[3] have studied the halogen derivatives of methane and have found the effects produced by the substitution of the halogens for hydrogen. The present investigation was undertaken to see what modifications are produced in the infra-red absorption bands of the methyl, ethyl, propyl and butyl groups by having a nitrate ion used instead of a single atom. Also, it is of interest to note the absorption spectrum of the nitrate ion in organic compounds so that it may be compared with the absorption spectrum of the nitrate ion in inorganic compounds.

Experimental Procedure

A Hilger infra-red spectrometer with a quartz prism was used from 1 to 2.6μ, the slit including about 0.02μ. The readings were taken at intervals of 0.02μ but the individual points are not shown on the curve to avoid crowding. The absorption cell was made by separating two pieces of glass with lead or

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[1] Cooley, Astrophys. J. **62,** 73 (1925).

[2] Dennison, Astrophys. J. **62,** 84 (1925).

[3] Easley, Fenner and Spence, Astrophys. J. **67,** 185 (1928).

lead foil. In this way cells of the necessary thickness could be obtained. From 2.6μ to 7.5μ a rock-salt prism was used, the effective slit width being about 0.07μ at 6.5μ. Microscope cover glasses were used for the windows of the cells from 2.6 to 4.5μ and then rock salt, cut and polished, was used from 4.5 to 7.5μ. No correction was made for the loss of intensity at the windows; this usually amounted to about 10 or 15 percent. In some cases it was found necessary to seal the windows on to the lead or foil and Le Page's glue was used for this purpose. Some cells were made with the glue and some without it, but no difference greater than would be expected due to observational errors was found between the two types of cells.

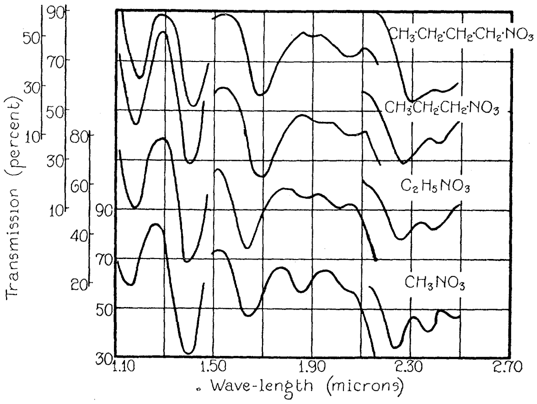

Fig. 1. The infra-red absorption spectra of methyl, ethyl, propyl and butyl nitrates from 1.1 to 2.5μ. The thickness of cells used: 15 mm from 1 to 1.5μ; 0.5 mm from 1.5 to 2.2μ; 0.3 mm from 2.2 to 2.5μ.

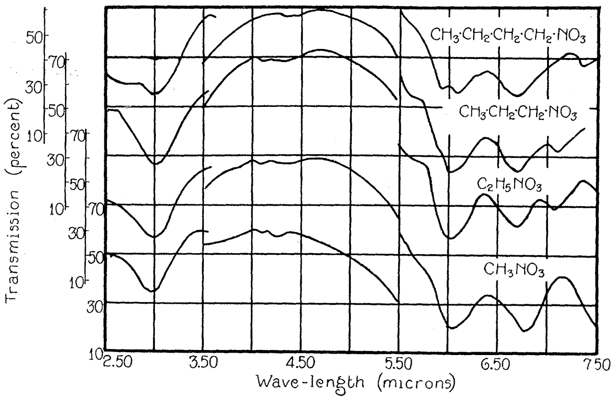

Fig. 2. The infra-red absorption spectra of methyl, ethyl, propyl and butyl nitrates from 2.5 to 7.5μ. The thickness of cells used: 0.12 mm from 2.5 to 5.5μ; 0.03 mm from 5.5 to 7.5μ.

The organic liquids for this work were prepared by standard methods in the chemical laboratory of the University of North Carolina. The liquids were dried over an excess of calcium nitrate until the vapor pressure of the liquid became equal to the vapor pressure of the drying agent. This was done to render the liquids water free. The liquids prepared for this study are methyl nitrate, ethyl nitrate, propyl nitrate and butyl nitrate.

RESULTS AND DISCUSSION

A complete curve for each liquid is given in Fig. 1 and in Fig. 2. Since the bands cannot be located from these curves with accuracy on account of the small scale used, a list of all bands observed is given in Table I.

TABLE I. *List of all observed absorption bands between 1 and 7.5μ.*

Methyl Nitrate	Ethyl Nitrate	Propyl Nitrate	Butyl Nitrate
1.16μ	1.18μ	1.18μ	1.20μ
1.40	1.40	1.40	1.42
1.64	1.64	1.68	1.70
1.86	1.86	2.06	2.06
2.02	2.02	2.28	2.30
2.24	2.26	2.40	2.44
2.36	2.38	2.58	2.58
2.48	2.54	3.02	3.02
2.96	3.02	4.30	4.28
4.12	4.34	6.04	5.92
4.30	6.04	6.70	6.10
6.02	6.70	7.06	6.70
6.74	7.06		6.88
			7.12

By comparing the curves certain characteristics are seen. The intensity of the bands decrease as the CH_2 group is introduced between the CH_3 and NO_3 groups. The first band, which occurs at 1.16, 1.18 and 1.20μ in the methyl, ethyl, propyl and butyl nitrates, respectively, has a percent transmission of 60 in the methyl, 50 in the ethyl, 45 in the propyl, and 35 in the butyl. The other intense bands, except those at 1.40μ and 2.96μ, decrease similarly in percent transmission as the complexity of the molecule is increased, although there is no uniformity in the amount of decrease. There is a very noticeable tendency of the bands to shift to longer wave-lengths as a CH_2 group is introduced. The first band observed in this work at 1.16μ in methyl nitrate shifts to 1.18μ in the ethyl and propyl nitrates and to 1.20μ in the butyl nitrate. This shift to longer wave-lengths occurs in the bands at 1.16, 1.64, 2.24, 2.36, 2.48 and 4.30μ in the methyl nitrate and corresponding bands in the other liquids.

The bands at 1.42μ and 2.96μ show very little change in intensity or in position for the different nitrates. This probably shows that these bands are produced in a different way from the characteristic bands of the CH linkage[4] which have just been noted. At first it was thought that these bands were produced by the nitrate ion. By the work of Schaefer and Schubert[5] the

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[4] In accordance with the custom of other observers some bands are attributed to energy changes of certain groups of atoms in the molecules (such as CH linkage). However, it is more accurate to consider each band as produced by an energy change of the molecule as a whole rather than by certain groups of atoms within the molecule.

[5] Schaefer and Schubert, Ann. d. Physik 577 (1918).

fundamentals of the bands of nitrate ion are about 7.3μ, 13.74μ and 15.58μ. We would expect to find overtones and combination bands in the near infra-red region. Since no bands of much intensity were observed between 3.5μ and 5.5μ, it must be concluded that the bands at 1.42μ and 2.96μ are not higher overtones or combination bands including overtones which may be attributed to the nitrate ion.

These bands may be attributed to a rearrangement within the molecule so that a hydrogen atom becomes associated with one of the oxygen atoms of the nitrate ion. This change within the molecule does take place in the NO_2 group and if present in nitrate ion would probably cause all the nitrate bands to be modified. If this re- arrangement takes place, there would be characteristic OH bands as found in alcohol. These bands occur for the alcohols at about 1.57 and 3.06μ.

The bands at 1.42μ and 2.96μ may also be due to a small amount of water left in the liquid when it was made or taken up by it from the air. From the work of Collins[6] the water bands in this region occur at 1.44μ, 1.95μ and 3.00μ for room temperature and Coblentz[7] has measured the water bands in the longer wave-length region to be at 4.75 and 6.00μ. In all the liquids an intense band was found at 6.00μ. There is considerable doubt as to what causes these bands may be attributed, but from their position in the spectrum and intensity t does not seem probable that they are produced by the CH linkage or the nitrate group.

It is remarkable that no bands which are very intense may be attributed to the nitrate ion. Only in the region from 7μ to 7.5μ are found bands which correspond to the inorganic nitrates. The intensity of these bands are much smaller than for the inorganic nitrates and it may be that these bands are not due to the nitrate ion but to the CH linkage. A 20 percent solution in water of potassium, calcium, lead and lithium nitrates in each case showed very intense bands with maxima of absorption occurring between 7.15 to 7.4μ for the different solutions. Pringsheim[8] has been able to get strong Raman lines which indicate a band at about 7.2μ for the nitrates in a solution of water.

It is evident that the nitrate ion in organic compounds does not produce bands at all similar to the nitrate ion in inorganic compounds. This difference in the two types of compounds is probably due to the influence of the CH group on the nitrate ion in the organic compounds.

An attempt has been made to classify the bands which may be attributed to the CH linkage. Ellis[9] made a study of a number of compounds and found that all the near infra-red bands of CH compounds could be attributed to overtones of the fundamental at 6.44μ. Barnes and Fulweiler,[10] and later

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[6] Collins, Phys. Rev. **26**, 771 (1925).

[7] Coblentz, Investigations of Infra-Red Spectra, Part 3, Page 17.

[8] Pringsheim, Zeits. f. Physik **50**, 741 (1928).

[9] Ellis, Phys. Rev. **27**, 298 (1926).

[10] Barnes and Fulweiler, Jour. Am. Chem. Soc. **49**, 2034 (1927).

Ellis,[11] showed that the band at 3.28μ must be an overtone. Easley, Fenner and Spence[3] found that it was necessary to assume four fundamental frequencies in order to account for the bands observed by them in the halogen derivatives of methane. One of the writers has shown that all organic liquids, containing carbon and hydrogen, which have been measured thus far have a system of bands in near infra-red with many similar characteristics. It was shown that if four fundamentals are assumed for the carbon-hydrogen compounds, all the more intense bands in the near infra-red can be arranged in a similar series by attributing the bands to the overtones and combinations of the fundamentals. In addition to this series there occurs in some compounds another series of bands which may be attributed to other groups within the molecule, such as an OH group. In Table II the close similarity between the different nitrates studied is readily seen. Due to the great intensity of the band at 3.00μ, the fundamental at about 3.35μ, ν_1, scarcely appears.

TABLE II. *Combinations of the intense observed bands.*

Methyl	Ethyl	Propyl	Butyl Nitrate	Combinations
obs.	obs.	obs.	obs.	
1.16μ	1.18μ	1.18μ	1.20μ	$3\nu_1$
1.64	1.64	1.68	1.70	$2\nu_1$
1.86	1.86			$\nu_1+\nu_2+\nu_3$
2.06	2.02	2.06	2.06	$\nu_1+\nu_3+\nu_4$
2.24	2.26	2.28	2.30	$\nu_1+\nu_2$
2.36	2.38	2.40	2.44	$\nu_1+\nu_3$
2.48	2.54	2.58	2.58	$\nu_1+\nu_4$
6.74	6.70	6.70	6.70	ν_2

The fundamental at 6.70μ, ν_2, has been observed in the four compounds and the position is almost the same for each one, but the complexity of this band increases as each CH_2 group is added.

Three intense bands have been observed at 2.24, 2.36 and 2.48μ in methyl nitrate and corresponding bands in the other nitrates. By comparison with the absorption bands of benzene and other organic liquids containing only carbon and hydrogen, these bands are attributed to the combinations $\nu_1+\nu_2$, $\nu_1+\nu_3$, and $\nu_1+\nu_4$, where ν_3 denotes the fundamental which has a wave-length from 8 to 12μ, and ν_4 the fundamental from 12 to 18μ.

The wave-length of ν_1 may be calculated from the two overtones observed at 1.16μ and 1.64μ for methyl nitrate and at corresponding positions for the other nitrates. Since only one of the fundamental bands has been observed in the experimental work, it was found that most of the observed bands must be considered also as calculated values in order to find the wave-length of the fundamentals. For this reason only the observed bands are given in Table II and the combination is assigned by analogy to the absorption spectra of other organic compounds. These combinations will be discussed more fully in a future paper which will treat of various types of absorption bands found in organic liquids.

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[11] Ellis, Phys. Rev. **31,** 310 (1928).