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Ultraviolet Absorption Spectra of Nitroparaffins, Alkyl Nitrates, and Alkyl Nitrites[1]

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Ultraviolet absorption spectra have been determined for a series of nitroparaffins, alkyl nitrates, and alkyl nitrites. The relationship between structure and absorption spectra has been discussed.

During an investigation of the chemistry of nitroparaffins, alkyl nitrates, and alkyl nitrites, the ultraviolet absorption spectra of a number of these compounds were determined. The experimental results are summarized and interpreted in the present communication.

Nitroparaffins. Aliphatic nitro compounds are characterized by a broad absorption band of low intensity in the region of 270–284 mμ and a second band of greater intensity which lies below 200 mμ.[4-7] The bands are usually well separated and distinct except in those nitro compounds where both oxygens of the nitro group are bonded with adjacent hydroxyl groups or one oxygen with an N—H group. In these cases the low-intensity band occurs only as a shoulder or inflection.[8] A maximum at 366 mμ, which is occasionally ascribed to the nitro group,[9,10] has not been observed in these compounds and presumably refers to one of the weak bands in nitrobenzene.[7]

The wavelength of the low-intensity transition of the aliphatic nitro compounds is relatively independent of the type of alkyl group.[6] The over-all variation in the 21 compounds examined is only 7 mμ (Table I). Within this range the primary nitro paraffins absorb at shorter wavelengths (274–278 mμ), the tertiary compounds near the upper limit (278–281 mμ), and the secondary compounds in between. The molar absorptivities, in general, have a tendency to increase with molecular weight. Nitro esters fit into the series, as do cyclic nitroparaffins. The behavior of the tertiary compounds and of 2-nitro-2-chloropropane makes it unlikely that steric effects play any considerable role in α-chloro nitroparaffins, as was proposed for chloropicrin.[6]

TABLE I

ABSORPTION SPECTRA OF NITRO COMPOUNDS IN ETHANOL

Compound	Type	λ_{max}, mμ	ϵ
1-Nitrobutane[a]	I°	276	24
1-Nitropentane[a]	I°	276	26
1-Nitrohexane	I°	275	28
1-Nitroheptane	I°	274	30
1-Nitroöctane	I°	276	29
1-Nitro-2-methylpropane	I°	277	31
1-Nitro-3-methylbutane[a]	I°	275	29
Cyclohexylnitromethane[b]	I°	278[a]	41
2-Nitropropane[c]	II°	276	27
2-Nitrobutane	II°	279	24.5
2-Nitroöctane	II°	277	34.5
Nitrocyclopentane[d]	II°	277	31
Nitrocycloheptane[d]	II°	276	39
Ethyl α-nitrobutyrate	II°	278	30
Ethyl α-nitrovalerate	II°	278	31
Ethyl α-nitrocaproate	II°	279	32
2-Nitro-2-methylpropane[b]	III°	278	25
1-Nitro-1-methylcyclopentane[b]	III°	279	31
1-Nitro-1-methylcyclohexane[b]	III°	280	32
2-Nitro-2,4-dimethylheptane[b]	III°	280	32
2-Nitro-2-chloropropane	III°	281	31

[a] Taub, PhD thesis, Purdue University, 1952. [b] Rimmer, PhD thesis, Purdue University, 1953. [c] In ether λ_{max} 278, ϵ_{22}. [d] Mooberry, PhD thesis, Purdue University, 1954.

The 280 mμ absorption band of aliphatic nitro compounds is shifted to the blue on increasing the polarity of the solvent. Thus nitromethane absorbs at 277.6 mμ in heptane, at 274 mμ in ethanol, and at 268.8 mμ in water while in 90% sulfuric acid the band occurs at 252.5 mμ.[7,11]

Alkyl nitrates. Various alkyl nitrates which have been investigated, show a weak band in ethanol at 270 mμ as a shoulder (Fig. 1). The position of the band and the shape of the curve are little affected by varying the alkyl group, while the molar absorptivities at 270 mμ for eight compounds vary from 15

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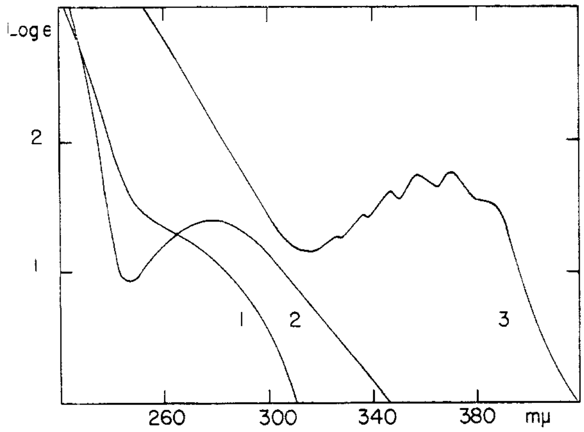

FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA: (1) 2-butyl nitrate in ethanol; (2) 2-nitrobutane in ethanol; (3) 2-butyl nitrite in ether.

to 37 without any obvious relationship to structure, except that II° alkyl nitrates of larger molecular weight have higher values (Table II). The absorption intensities and wavelengths agree with other measurements.[4,6]

TABLE II

ABSORPTION SPECTRA OF ALKYL NITRATES IN 95% ETHANOL

Compound	Type	ϵ_{270} mμ
Cyclopentylmethyl nitrate[a]	I°	16
Cyclohexylmethyl nitrate[a]	I°	20
1-Octyl nitrate	I°	15
2-Butyl nitrate	II°	17
Cyclohexyl nitrate[a]	II°	22
4-Heptyl nitrate	II°	28
2-Octyl nitrate	II°	37
5-Methyl-2-octyl nitrate	II°	33

[a] Rimmer, PhD thesis, Purdue University, 1953.

Alkyl nitrites. Alkyl nitrites exhibit two maxima above 200 mμ, a high-intensity band at 228 mμ and a low-intensity transition with six or seven vibrational fine-structure bands centered at around 375 mμ (ε about 70)[6,7,12,13] (Fig. 1). The solution spectra of alkyl nitrites in the region of 300–400 mμ are characteristic for each type and permit the rapid identification of primary, secondary, and tertiary nitrites (Fig. 2). Within each group of nitrites the wavelengths of the fine structure bands change little except when the electronic character of the *alpha* carbon is changed, an increase in the electron density of this carbon producing a shift of all bands to the red and an increase in the absorption intensity. The molar absorptivities tend to increase with the molecular weight of the alkyl group (Table II).

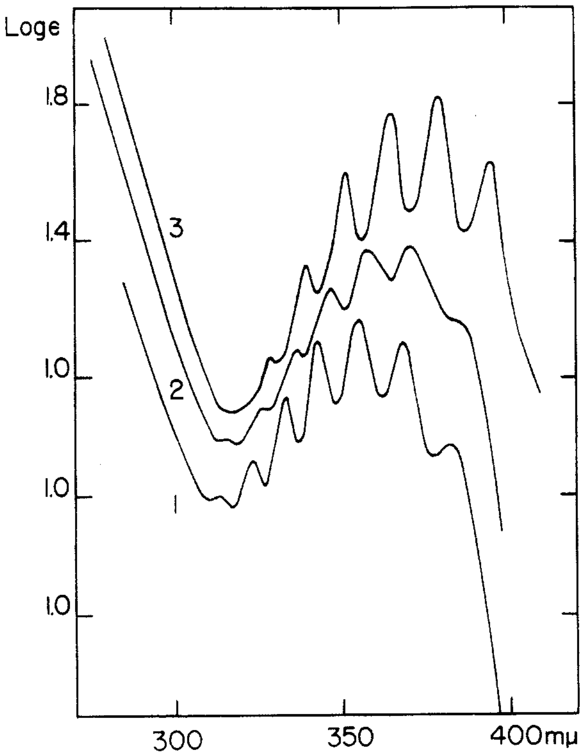

FIG. 2.—ULTRAVIOLET ABSORPTION SPECTRA IN ETHER: (1) isobutyl nitrite; (2) *sec*-butyl nitrite; (3) *tert*-butyl nitrite.

As in the case of the nitro compounds, the weak transition in the alkyl nitrites may be regarded as blue shift band[14] since the band farthest to the visible of *tert*-butyl nitrite, for instance, is shifted from 398.2 mμ in vapor[15] to 395 mμ in ethanol, and to 383 mμ in water (Table III). Changes in the polarity of the solvent probably also change the ratio of *cis*- and *trans*-isomers.[16]

Applications. The ultraviolet absorption spectra of nitroparaffins, alkyl nitrates, and alkyl nitrites differ sufficiently (Fig. 1) so that they can be used for identification purposes for pure compounds. Recently the ultraviolet absorption above 400 mμ has been utilized for determining alkyl nitrites in Victor Meyer reaction mixtures also containing alkyl nitrates and nitroparaffins.[17] Since nitro compounds and nitrates do not absorb in this region (Fig. 1), the ether solution of the products, made up to a definite volume, can be read directly after removing the silver salts from the reaction mixture. Some caution is necessary with this method since it has been observed that nitrogen dioxide in ether absorbs in the same region as the nitrites, having

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TABLE III

ULTRAVIOLET ABSORPTION SPECTRA OF ALKYL NITRITES IN ETHER

Isobutyl	λ 313	323	332.5	343	355	368	382
	ε 22.6	29.0	44.8	64.7	76.1	64.7	31.6
n-Hexyl[a]	λ 314	323.5	333.5	344	356	368.5	382
n-Heptyl	λ 314.5	323.5	333	344.5	356	369	382.5
	ε 23.7	32.4	51.4	73.0	84.7	69.9	32.9
n-Decyl[a]	λ 314.5	323.5	333	344	356	369	383
2-Phenyl-1-propyl	λ 315	323	332.5	344	355	368	382
	ε 29.8	34.3	49	69.5	82.9	69.4	40.8
Benzyl	λ 315	325.5	336	346	357	370	385[b]
	ε 23.4	27.6	39.1	54.2	63.1	55.8	28.5
p-Methylbenzyl	λ 315[b]	327	337	348	359	370	
	ε 28.2	31.8	45.1	61.1	71.6	63.3	
p-Methoxybenzyl	λ 318	328	339.5	351	361	373[b]	
	ε 11.0	45.7	55.6	71.0	80.4	72.7	
2-Propyl	λ	327	337	347	359	373	387
	ε	15.8	25.2	38.6	50.5	49.3	28.0
2-Butyl	λ	327	336	346	357	369	382
	ε	18.1	26.9	40.8	54.3	55.8	35.2
2-Octyl	λ	326	336	346	357	369	382
	ε	19.7	29.6	44.7	60.2	61.6	39.1
1-Phenyl-2-propyl	λ	325	336	346	356	368	380
	ε	21.5	30.5	45.4	61	65.6	46.1
tert-Butyl[c]	λ	329	340	352	365.5	379.5	395
	ε	11.5	21.4	40.5	61.0	68.6	43.6
tert-Amyl	λ	329	341	353	365.5	380	394.5
	ε	11.6	21.5	38.1	57.3	63.7	40.0

[a] The exact concentration was not determined in this case.

[b] Shoulder.

[c] In water	327[b]	335	346	357	369	383
In vapor[d]	—	339	351.8	365.8	381.1	398.2

[d] Tarte, *J. Chem. Phys.*, 20, 1570 (1952).

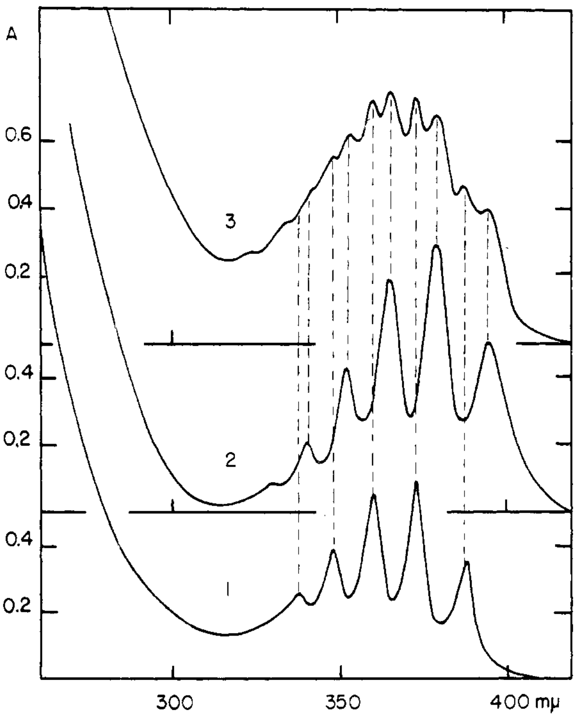

FIG. 3.—ULTRAVIOLET ABSORPTION SPECTRA IN ETHER: (1) NO_2; (2) *tert*-butyl nitrite; (3) *tert*-butyl nitrite containing NO_2.

five vibrational fine-structure bands at 337, 348, 359, 373, and 387 mμ. These absorption bands are sufficiently displaced with respect to the nitrites so that they appear as shoulders or separate bands in mixtures of nitrites and nitrogen dioxide in ether (Fig. 3). The interfering absorption bands can be detected by scanning the region between 300 and 400 mμ with a recording spectrophotometer.

In view of the great differences in the spectra of primary, secondary, and tertiary nitrites, it has been possible to ascertain that isobutyl nitrite is identical whether it is prepared from the alcohol by means of sodium nitrite and aluminum sulfate[18] or by use of nitrosyl chloride in pyridine, and that it is formed from isobutyl halides and silver nitrite without isomerization. The spectra of the isomeric phenylpropyl nitrites differ sufficiently so that they can be used for determination of mixtures. As little as 5% (or less) of the secondary nitrite can be detected in mixtures of known concentration. Since the ultraviolet spectra of the nitrites from the Victor Meyer reactions[19] are identical with those prepared from the alcohols by reaction with nitrosyl chloride in pyridine, it may be concluded that no appreciable isomerization occurred. Rearrangements of nitrites have not been encountered in any of the Victor Meyer reactions investigated.

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EXPERIMENTAL

Starting material. The preparation and separation of the nitro compounds, nitrates, and nitrites, have been described previously in detail.[17,19] The purity of each of the substances was established by means of infrared absorption spectra. Nitrogen dioxide in ether was obtained by dissolving purified nitrogen tetroxide in anhydrous ether and diluting successively until the absorbencies were brought into range.

Ultraviolet absorption spectra for alkyl nitrates and nitro compounds were determined in 95% ethanol, those for alkyl nitrites in anhydrous ether to avoid ester interchange reactions with alcohol. The measurements were made in 1-cm. cells at 25° with a Cary recording spectrophotometer.[20]

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(20) Measurements by Robert P. Curry, Purdue University.