THE ABSORPTION SPECTRA OF NITROGLYCERINE.

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The absorption spectra of nitroglycerine have been studied with a view to a further study of the modes of photochemical decomposition.

In 1919, Harry Hepworth⁽¹⁾ obtained the absorption spectra of the nitric esters of glycerol to make clear that there is no evidence of chemical isomerism in solution, and that the labile and stable solid forms of nitroglycerine are to be regarded as physical isomerides. And therefore it has been only found that all of the nitric esters of glycerine showed end absorption almost linear between 40000 $cm.^{-1}$ and 47000 $cm.^{-1}$

From the consideration of the some nitrocompounds and nitroesters, the selective absorption of nitroglycerine should appear from the concentration of N/10 in the ordinary thickness (from 1 mm. to 100 mm.) and therefore it could not be discovered by Hepworth, since the solubility in water used by him as a solvent prevented to obtain a concentration higher than N/20000.

The author's investigations have been done for a considerable range of concentration and thickness from 50 cm. of nitroglycerine in liquid to 1 mm. of N/1000 alcoholic solution. The results are in a good agreement with his prediction.

Experimental. The experiments were made with nitroglycerine prepared in the laboratory, washed with successive changes of distilled water, dried in vacuum over solid potassium hydroxide, and finally obtained as a clear, mobile, faint yellow oil which froze at 12.6°C.; sp. gr. 1.5958 at 25°C.

The absorption of a column of nitroglycerine in liquid and in alcoholic solution for a suitable concentration and thickness of layer previously described was examined with Hilger E_2 spectrograph. A hydrogen discharge tube constructed by the author was used as a source of continuous light. Photographic plates employed were the Ilford soft gradation panchromatic plates and the Schumann plates for the short wave length. The time of exposure was five minutes. The results are given in Table 1 and the curve of the absorption is shown in Fig. 1.

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(1) *J. Chem. Soc.*, **115** (1919), 840.

Table 1. Nitroglycerine.

Logarithms of thickness				Wave length	Wave number
		log *D*	log *D*(3)	λ (Å)	ν (mm.$^{-1}$)
Pure liquid(2)		2.70	7.02	4227	2365
		2.23	6.55	3767	2654
		2.00	6.32	3586	2788
		1.00	5.32	3214	3115
Alcoholic solution	1 N	2.00	5.48	3263	3061
		1.80	5.28	3225	3100
		1.60	5.08	3191	3133
		1.40	4.88	3161	3163
		1.20	4.68	3126	3198
		1.00	4.48	3117	3207
	N/10	2.00	4.48	3117	3207
		1.80	4.28	3076	3250
		1.60	4.08	3031	3298
		1.40	3.88	2973	3363
		1.20	3.68	2907	3439
		1.00	3.48	2838	3523
		0.80	3.28	2748	3639
		0.70	3.18	2696	3708
		0.60	3.08	2612	3827
		0.50	2.98	2493	4010
		0.40	2.88	2449	4082
		0.20	2.68	2405	4157
		0.00	2.48	2374	4211
	N/100	2.00	3.48	2830	3533
		1.90	3.38	2778	3599
		1.70	3.18	2695	3703
		1.50	2.98	2492	4012
		1.40	2.88	2471	4046
		1.20	2.68	2439	4116
		1.00	2.48	2385	4192
		0.70	2.18	2325	4300
		0.50	1.98	2282	4381
		0.20	1.68	2230	4483
	N/1000	2.00	2.48	2384	4193
		1.95	2.43	2370	4218
		1.70	2.18	2325	4300
		1.50	1.98	2285	4375
		1.40	1.88	2272	4400
		1.20	1.68	2230	4483
		0.90	1.38	2178	4590
		0.50	0.98	2105	4749

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(2) Since the density of nitroglycerine is 1.60, pure liquid corresponds to 7.05 N.

(3) For convenience of comparison of the spectra, the author took one gram mol divided by the number of NO_2 group for one gram mol; in the case of nitroglycerine it is equal to the molecular wt. divideded by 3.

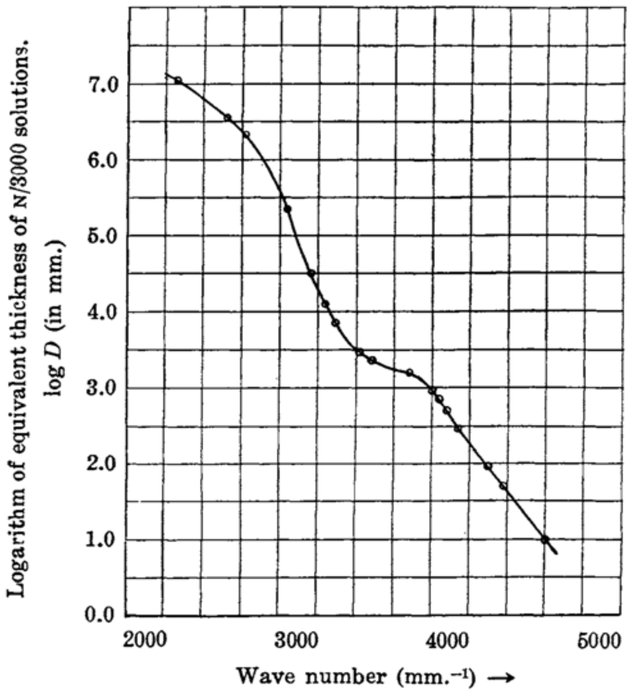

Fig. 1. The Absorption Spectra of Nitroglycerine.

Discussion. The first and probably the second absorption bands of nitroglycerine may be reasonably to attributed to the NO_2-groups in the molecule, since the absorption spectra of the simple nitrocompounds and also nitric esters lacking other special groups (except NO_2) which not only have an absorption at wave length greater than 2000 Å, but also show irregularity of the band owing to the effect of an intense polarity, are quite similar in type. The absorption bands of these compounds, namely, nitromethane,(4)(5)(6) nitroethane,(4)(6)(7) nitropropane,(6) 2-nitro-propane,(6) nitrocyclohexane,(6) 1-methyl-1-nitro-cyclopentane,(6) nitric acid,(8) ethyl nitrate,(7) are almost the same at the wave lengths ca. 3200–2500 Å and less than 2500 Å and also similar in the intensity as Table 2 shows.

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(4) Baly, *J. Chem. Soc.*, **93** (1908), 1747.
(5) Hedley, *Ber.*, **41** (1908), 1195.
(6) Zelinsky and Rosanoff, *Z. physik. Chem.*, **78** (1912), 629.
(7) J. W. Goodeve, *Trans. Faraday Soc.*, **30** (1934), 504.
(8) P. Bovis, *Ann. phys.*, **10** (1928); *Compt. rend.*, **178** (1924), 1964; *ibid.*, **185** (1928), 57.

Table 2. The 1st Absorption Bands of Nitrocompounds and Nitroesters.

Compound	Wave length (Å)	Max. (Å)	Intensity (log ε)*
Nitromethane	3000—2500	2700	1.2
Nitroethane	3300—2500	2760	1.1
Nitropropane	3100—2500	2760	1.0
2-Nitropropane	3100—2500	2740	1.1
Nitrocyclohexane	3200—2500	2780	1.1
1-Methyl-1-nitrocyclopenthane	3200—2500	2810	1.2
Nitric acid	3100—2500	2700	1.0
Ethyl nitrate	3100—2500	2700	1.0
Nitroglycerine	3300—2500	—	1.0

* ε is the molecular extinction coefficient.

From the results, these two diffused bands common to the nitrocompounds and nitroesters may be attributed to the NO_2-group in which the valency-electronic jumps accompanied by molecular vibration may be expected. The general discussion will be given in another paper.

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