451. *Infrared Spectra and Structure of Nitrates of Some Aldehydes, Ketones, and Ethers.*

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Infrared spectra have been examined of the addition compounds (" nitrates ") of aldehydes, ketones, and ethers with nitric acid. The spectra give a broad band at 2700—2600 cm.$^{-1}$ which can probably be assigned to the hydroxonium bond ($=O^{+}-H$) and a strong band near 1400 cm.$^{-1}$ produced by the NO_3^- ion. It is concluded that the nitrates possess mainly an ionic structure, $>C=O^{+}H\ NO_3^{-}$ (for aldehydes and ketones) or $\begin{matrix}C\\C\end{matrix}\!>O^{+}H\ NO_3^{-}$ (for ethers).

It has been known since 1835 that many organic compounds containing a carbonyl group, such as aldehydes and ketones, form addition products with nitric acid.[1] They have since been described by numerous authors.[2-5] Reddelien,[6] who carried out particularly extensive studies, represented the structure diagrammatically as $>C=O \cdots HONO_2$ which in modern terms would denote combination by an intermolecular hydrogen bond. The structure of these addition products (which we shall call " nitrates ") has now been examined by infrared spectroscopy.

Nitrates of isobutyraldehyde, benzaldehyde, and cinnamaldehyde, acetone, isobutyl methyl ketone, di-n-butyl ketone, acetophenone, and benzophenone were prepared and examined. It has also been now suggested that the structures of the addition compounds of ethers with nitric acid[7] are similar to those of the nitrates of aldehydes and ketones. We also examined the infrared spectra of a few ethers (di-n-butyl ether, 1,4-dioxan, and tetrahydrofuran). Also 2,6-dimethylpyrone nitrate has been prepared and its spectrum examined. Further it proved necessary to study the infrared spectra of nitric acid of various concentrations.

EXPERIMENTAL

Aldehyde and Ketone Nitrates.—The addition products of aldehydes and ketones with nitric acid were prepared in principle as described by Reddelien,[6] but the aldehyde or ketone

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[1] Dumas and Peligot, *Annalen*, 1835, **14**, 65.

[2] Mulder, *Annalen*, 1840, **34**, 165; Kehrmann and Mattisson, *Ber.*, 1902, **35**, 343; Schmidt and Bauer, *Ber.*, 1905, **38**, 3758.

[3] Kachler, *Annalen*, 1871, **159**, 283.

[4] Collie and Tickle, *J.*, 1899, **75**, 710.

[5] Meyer, *Ber.*, 1910, **43**, 157.

[6] Reddelien, *Ber.*, 1912, **45**, 2904; 1915, **48**, 1462; *J. prakt. Chem.*, 1915, **91**, 213; *Angew. Chem.*, 1922, **35**, 580.

[7] McIntosh, *J. Amer. Chem. Soc.*, 1905, **27**, 1013.

(1 mol.) was added dropwise to nitric acid (99·5%; 1 mol.) while the temperature was kept at −40° to −50°. The products were separated as oils or crystals. Only the lower part of the oily layer was used for analysis and spectroscopy. The crystalline addition products were separated by filtration on a cooled funnel (−50°) and purified by being pressed on a porous plate cooled with solid carbon dioxide. The content of nitric acid was determined by titration.

TABLE 1.

Nitrates of organic compounds.

Organic component	Yield (%)	M. p.	Formula	HNO_3 (%) Found	HNO_3 (%) Reqd.
Benzaldehyde [6]	89	−12°	C_7H_6O,HNO_3	38·0	37·0
Cinnamaldehyde [1, 2]	91	+60	C_9H_8O,HNO_3	32·8	32·3
Acetone [7]	92	−18	C_3H_6O,HNO_3	52·2	52·0
Acetophenone [6]	91	−24	C_8H_8O,HNO_3	33·6	34·4
Benzophenone [5, 6]	89	+31	$C_{13}H_{10}O,HNO_3$	25·3	25·7
2,6-Dimethylpyrone [4]	88	+9	$C_7H_8O_2,2HNO_3$	50·6	50·4
Isobutyraldehyde	92	−24	C_4H_8O,HNO_3	45·6	46·7
Isobutyl methyl ketone	91	Oil	C_6H_{12},HNO_3	38·1	38·65
Di-n-butyl ketone	93	−45	$C_9H_{18}O,HNO_3$	30·1	30·7
Di-n-butyl ketone	91	Oil	$C_8H_{18}O,HNO_3$	32·3	32·5
1,4-Dioxan	89	+11	$C_4H_8O_2,2HNO_3$	58·2	58·9

Ether Nitrates.—The addition products of ethers and nitric acid were prepared in the same way, similar to that indicated by McIntosh.[7] The product from tetrahydrofuran was also prepared but was unsuitable for investigation as it decomposed with violence shortly after being prepared.

TABLE 2.

Infrared frequencies of aldehydes and their nitrates.

Isobutyraldehyde		Benzaldehyde		Cinnamaldehyde		
aldehyde	nitrate	aldehyde	nitrate	aldehyde	nitrate	Assignment
	3130w		3100m			OH of nitric acid
		3071		3057w		C–H stretching in aromatic ring
				3024w	3000m	C–H stretching in alkenes
2967m	2967m					C–H stretching of CH_3, CH_2, and CH
2929sh	2929sh					
2868m	2868m	2854sh	2873w			
		2821m		2807m		C–H stretching vibrations in aldehydes
		2741m		2731m		
2708w		2706w				
	2690mb		2600mb		2330wb	$=O^+–H$
1703s	1670s	1703s	1670s	1670s	1651s	C=O
				1623s	1618s	
		1599m	1604m	1599sh	1590sh	C–C aromatic skeletal in-plane
		1585m	1580m	1571w		
1472m	1466sh	1458m	1481sh	1490w	1443s	
1415w		1391m		1448m		
				1396w		
	1375s		1401s		1395s	NO_3^-
1330w		1316m		1330w		
	1300s		1307s		1290s	NO_2
1292w		1288w		1260w	1257s	
1241m		1268s				
1208sh	1208sh		1212m			
1160w	1160w	1189m	1170m	1160w	1163w	
				1123s		
1099w	1100w	1080w	1076w	1075w		
		1024w	1024w			
		1005w		1009w	988m	
				973s	960s	C=C
934m	943s	924w	944s			C–H deformation vibrations in aldehydes
844w		830m	835m		868w	
807w	815w				854w	
		750s	750s	750s	750s	C–H aromatic out-of-plane vibrations

Nitric Acid.—Nitric acid (98—99·5%) was prepared by distillation of a 1 : 2 v/v mixture of nitric acid (*d* 1·5) and sulphuric acid (99—100%) under reduced pressure. It was free from nitrogen dioxide.

Some properties of the nitrates are listed in Table 1. Nitrates for which references are not given are new.

Spectra.—Infrared absorption spectra were determined by means of a Hilger H-800 double-beam spectrophotometer with a 60° prism of sodium chloride. The liquid substances were used in capillary thicknesses, the solids as Nujol mulls. To avoid corrosion of the cuvettes, they were prepared from silver chloride.[8]

A technique for preparation of perfectly polished plates of pure silver chloride will be described elsewhere.[9]

As some of the substances are hygroscopic, they were also examined in Polyethylene envelopes.

The addition products were taken for analysis and spectroscopic examination immediately after preparation. This was important as some of them are unstable at their m. p. and above.

The frequencies were checked by means of a polystyrene film. The frequencies are recorded in Tables 2—6.

DISCUSSION

Hydroxyl Stretching Vibrations.—Some of the nitrates show a broad band of low or medium intensity in the region 3130—3060 cm.$^{-1}$. This is probably produced by the hydrogen-bonded hydroxyl group present in the molecule of free nitric acid. The latter can be present in the substances in traces owing to the relative instability of some of them at room temperature.

TABLE 3.

Infrared frequencies of ketones and their nitrates.

Acetone		$Bu^i·CO·Me$		Bu^n_2CO		Acetophenone		Benzophenone		
ketone	nitrate	ketone	nitrate	ketone	nitrate	ketone	nitrate	ketone	nitrate	Assignment
	3090m		3080w		3094w		3080w		3060w	OH of nitric acid
3010m						3075m				
						3009w				
2930m	29	2973s	2962s	2958s	2962s	2925w	2940w			Aliphatic C–H stretching
				2939s	2939s					
		2868s	2873s	2873m	2873m					
	2640s		2665s		2679m		2660m		2660w	$=O^+–H$
	2415m		2311w				2330m			
1712s	1684s	1708s	1670s	1712s	1665s	1680s	1665s	1646s	1646s	C=O
						1598m	1598s	1594m	1594m	C–C ar. skeletal in-plane
						1580m	1580m	1571m	1571m	
1440sh		1472m	1467m	1462m	1459m	1448s	1448s	1448m	1448m	
1424m	1415sh	1424m								
		1406m		1410m						
	1387sh		1386s		1387s		1406s		1396m	NO_3^-
				1377m		1360s	1368s	1377m		
1360s	1339s	1363s	1363s			1307m		1316s	1316m	
	1287s		1297s		1302s		1292s		1288s	$O–NO_2$ symm.
1222s	1245sh	1241m	1203m	1259w		1260s		1278s		
		1174s		1165w	1165w	1189m	1184m	1179w	1179w	
1100m	1100m	1118w	1118w	1132m	1132w	1110sh	1100sh	1151w	1151w	
						1085m	1080w	1075w	1075w	
				1047m	1047m	1024m	1028m	1028m	1028m	
						1000sh	1000sh	1000w	1000w	
940w	940w	948m	943m			958s		948m		
					929s	925sh	934s	939m	939m	
								920m	920m	
		935w	827w			850w	860sh	811w	811w	
						760s	764s	769m	769m	C–H ar. out-of-plane deformation
						684m	684m			

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[8] Le Sech, *Chim. Analyt.*, 1958, **40**, 425.

[9] Hofman and Stefaniak, *Roczniki Chem.*, in the press.

TABLE 4.

Infrared frequencies of ethers and their nitrates.

Di-n-butyl ether		1,4-Dioxan		
ether	nitrate	ether	nitrate	Assignment
			3116b	OH in HNO_3
2952s	2960s	2972m	2987sh	C–H stretching in CH_3 and CH_2 groups
		2921sh	2935m	
2868s	2876s	2863m	2882sh	
	2600b		2650b	$=O^+–H$
	1845bw			
	1657s		1670s	$O–NO_2$ stretching antisym.
1464s	1460s	1453m		CH_2 scissor
	1422		1399sh	NO_3
1379s	1381s	1368w	1373s	
1303w	1298s		1303s	NO_2 stretching symm.
1235w		1291m	1260m	
		1258s		
1123s	1086s	1122s	1118	C–O–C in ethers
1042m		1085m	1083m	
		1049w	1045w	
980				
	932s		940s	NO_2 bending in NO_3^-
		889sh	894w	
		876s	866s	
835w	835w		828w	
740w	740w		776w	

C–H *Stretching Vibrations.*—The aromatic C–H vibrations are undetectable for the nitrates, as is the C–H stretching vibration of CHO group in aldehyde nitrates.

Band at 2690—2600 cm.$^{-1}$.—This is a broad band of medium intensity most typical for the nitrates. It is not present in aldehydes, ketones, or ethers and should probably be assigned to the hydroxonium bond $=O^+–H$. This would be on similar lines to the work by Ferriso and Hornig[10] who assigned such bands at 2570 and 2610 cm.$^{-1}$ for

TABLE 5.

Infrared frequencies of 2,6-dimethylpyrone and its dinitrate.

2,6-Dimethylpyrone		
pyrone	dinitrate	Assignment
	3090mb	OH of HNO_3
3048mb		
	2500sb	$=O^+–H$
1859w	1859m	
1670s	1651s	C=O
1613s		
1602sh		
	1557s	
	1498s	
	1361s	NO_3^-
1340s		
	1296s	NO_2 stretching symm.
1199m	1188m	C–O–C in the ether
1162sh		
1040m	1038w	
956w	941m	
927m	914m	
903s		
	875m	
	839w	
	776w	NO_3^-
	720w	

TABLE 6.

Infrared frequencies of nitric acid.

HNO_3 Concentration (%)			
99·5	98·2	6	Assignment
3375b	3385b	3400sb	OH hydrogen bonded
1665m	1665m	1642s	NO_2 stretching assym.
1368s	1368s	1385s	NO_3^-
1306m	1297m		NO_2 stretching sym.
930w	938w		NO_2 banding
835w	835w	829m	NO_3^-
772w	774w	770w	NO_3^-

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[10] Ferriso and Hornig, *J. Amer. Chem. Soc.*, 1953, **75**, 4113.

hydroxonium chloride and bromide, respectively. Rasmussen, Tunnicliff, and Brattain [11] moreover, assigned a band 2703 cm.$^{-1}$ to the resonance structure involving hydroxonium ion: $>C=O \cdots H^+ \longleftrightarrow >C=O^+{-}H$.

In the spectrum of cinnamaldehyde nitrate the frequency is considerably lower (2330 cm.$^{-1}$), perhaps owing to conjugation of the C=O group with double bonds of the side chain and the aromatic ring.

A band of the same frequency is present for the nitrates of the ethers examined (2650—2600 cm.$^{-1}$) and for the 2,6-dimethylpyrone dinitrate (2500 cm.$^{-1}$).

C–O *Stretching Vibrations.*—The bands at 1712—1646 cm.$^{-1}$ present in the spectra of all the aldehydes and ketones should be assigned to C=O stretching vibrations. Their frequencies are lower for the nitrates of non-aromatic aldehydes and ketones by 33 and 28—47 cm.$^{-1}$, respectively. They are also lower for the nitrates of the aromatic aldehydes investigated and for acetophenone, 19—33 and 15 cm.$^{-1}$, respectively. The frequencies are unchanged for benzophenone nitrate.

The difference between aliphatic and aromatic substances may be due to conjugation of C=O group with the aromatic rings. In benzophenone and its derivatives the two aromatic rings are in different planes, and it is possible to envisage competitive conjugation of two aromatic rings with the carbonyl group.

Both cinnamaldehyde and its nitrate give two strong bands in the C=O region, 1670, 1623 and 1651, 1618 cm.$^{-1}$, respectively, possibly due to the presence of *cis–trans*-isomers of cinnamaldehyde.

Band at 1422—1361 *cm.*$^{-1}$.—This strong band is present in the spectra of all the nitrates and of nitric acid and should be assigned to vibrations of the anion NO_3^-.

Antisymmetrical and Symmetrical NO_2 *Stretching Vibrations.*—The bands produced by the antisymmetrical stretching vibrations of the nitro-group of the nitric acid in the addition compounds could only be detected for the ethers, at 1670—1657 cm.$^{-1}$. With both aldehydes and ketones it was shielded by strong C=O vibrations. On the other hand, the bands due to symmetrical nitro-vibrations are prominent in spectra of all the nitrates examined.

Ether Bond C–O–C *Stretching Vibrations.*—Bands at 1123—1122 cm.$^{-1}$ in the spectra of ethers (Table 5) should be assigned to C–O–C vibrations. For the nitrates they are shifted to lower frequencies (1086 and 1118 cm.$^{-1}$). A much smaller shift was recorded for 1,4-dioxan. For 2,6-dimethylpyrone, the band at 1199 cm.$^{-1}$ should probably be assigned to the C–O–C bond; it is transformed into one at 1188 cm.$^{-1}$ in the spectrum of the dinitrate of this compound. The band at 1162 cm.$^{-1}$ for the free dimethylpyrone disappears from the spectrum of the nitrate.

Nitric Acid Spectra.—So far only a few papers have been published on the infrared spectroscopy of nitric acid.[12,13] With both concentrated and dilute nitric acid a strong band at 1368 cm.$^{-1}$ is found. This corresponds to the NO_3^- ion.[13] The weak bands at 835 and 774 cm.$^{-1}$ should also be assigned to this ion. The NO_2^+ band (2360 cm.$^{-1}$) was not detected for capillary layers.[13] All the nitro-group stretching vibrations (both antisymmetrical and symmetrical) are present in the spectrum with the frequencies typical for *O*-nitro-compounds. Also, concentrated nitric acid shows a weak band frequency 948 cm.$^{-1}$ which should be assigned to NO_2 bending vibrations.

The spectrum of the dilute acid contains a prominent hydroxyl band.

The authors are much indebted to Mrs. U. Dąbrowska for measuring the infrared spectra.

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[*Received, November 2nd*, 1961.]

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[11] Rasmussen, Tunnicliff, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

[12] Frejacques, *Compt. rend.*, 1952, **234**, 1769; Bethell and Sheppard, *J. Chem. Phys.*, 1953, **21**, 1421; Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.

[13] Marcus and Fresco, *J. Chem. Phys.*, 1957, **27**, 564.