332. *The Nitrous Acid–Tributyl Phosphate Complex.*

By J. M. Fletcher, D. Scargill, and J. L. Woodhead.

Tributyl phosphate extracts nitrous acid almost quantitatively from aqueous solutions. The spectrum, from 320 to 400 mμ, shows the enhanced fine structure characteristic of molecular nitrous acid and of alkyl nitrites. Distribution data indicate a 1 : 1 complex, $[Bu_3PO_4,HO{\cdot}NO]$, and infrared spectra that the hydrogen-bonding to the phosphoryl-oxygen atom modifies the bonding in nitrous acid towards an ionic structure.

It is known, from work on tributyl phosphate as a solvent for the extraction of metal nitrates from aqueous nitric acid, that nitrous acid formed in the system by thermal or radiolytic reactions is largely taken up by the organic phase. We have now been able to establish the nature of the complex responsible for the abnormally high distribution coefficient (*q*) of nitrous acid (compared with the coefficients of other acids). The stability of the complex is so great that, even in the presence of traces of water, solutions of up to M-nitrous acid may be prepared in tributyl phosphate.

The ultraviolet spectra of these solutions of nitrous acid in water-saturated tributyl phosphate show five sharp bands (Table 1) between 320 and 400 mμ. These can be attributed to molecular nitrous acid, since similar though weaker bands occur in the spectra of nitrous acid both as vapour[1] and when dissolved[2] in concentrated sulphuric, perchloric, and phosphoric acid. As Beer's law is obeyed (from 10^{-2} to 5×10^{-4}M-acid) it is concluded that the nitrous acid is present entirely in the molecular form.

TABLE 1. *Absorption spectra of nitrous acid in 100% tributyl phosphate.*

$\lambda_{max.}$ (mμ)	339		349·75		361·5		375·5		391
$\Delta\nu_{max.}$ (cm.$^{-1}$)		910		930		1030		1050	
$\lambda_{min.}$ (mμ)		343·5		355		368		382·5	
ε	29	18·5	54	22·5	83	23·5	96	16·5	57

TABLE 2. *Changes in q*(HNO_2) *with tributyl phosphate concentration.*

Total HNO_2 = 0·0125M; $HClO_{4\ org.}$, *ca.* 10^{-2}M.

Bu_3PO_4 (M)	0·025	0·05	0·075	0·10	0·15
$q(HNO_2)$ (org./aq.)	0·23	0·5	0·8	1·2	2·1

TABLE 3. *Infrared spectra of nitrous acid and methyl nitrite* (*in cm.*$^{-1}$).

HNO_2 in 100% Bu_3PO_4	HNO_2 in 10—20% Bu_3PO_4	HNO_2 vapour [a]	MeO·NO vapour [b]	Assignment	HNO_2 in 100% Bu_3PO_4	HNO_2 in 10—20% Bu_3PO_4	HNO_2 vapour [a]	MeO·NO vapour [b]	Assignment
3055	3065	3590		*trans* } O–H	1402	1391	1292		*cis* } O–H
2733	2736	3426		*cis* } stretch	—[c]	1306	1260		*trans* } bend
1629	1633	1696	1681	*trans* } N=O	926	941	856	844	*cis* } N–O
—[c]	1591	—[d]	1625	*cis* } stretch	881	872	794	814	*trans* } stretch

[a] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **12**, 1599. Tarte, *ibid.*, 1952, **20**, 1570. Obscured by Bu_3PO_4. [d] Obscured by NO_2.

The slope of the curve obtained when log *q*, for traces of nitrates, is plotted against log [Bu_3PO_4] has been used,[3] for up to 5% (0·18M) tributyl phosphate in inert diluents, to determine the composition of the complex in the organic phase. The limiting slope of the corresponding curve for $q(HNO_2)$ (Table 2) indicates that one molecule of tributyl phosphate is associated with one of nitrous acid and suggests that the complex has the composition Bu_3PO_4,HNO_2. The absence of significant absorption bands of water in the infrared spectra of 10—20% solutions of the phosphate, both with and without nitrous acid, shows that the complex does not contain water.

The complex shows a duplication (Table 3) of the infrared absorption bands of nitrous acid which can be attributed to *cis*- and *trans*-rotational isomers as in nitrous acid vapour[4] and alkyl nitrites.[5] In all three cases the bands of the *trans*-isomers are the more intense. The infrared frequencies (Table 3) of the N=O bands are substantially lower, and those of the N–O bands substantially higher, for Bu_3PO_4,HNO_2 than for nitrous acid vapour and methyl nitrite. This indicates a trend towards equivalence of the two nitrogen–oxygen bonds such as occurs in nitritometal complexes where these frequencies become[6] 1460 and 1065 cm.$^{-1}$ respectively. Associated changes (Table 3) in the O–H frequencies from those in nitrous acid vapour, and in the P=O frequency (Table 4) from that in tributyl phosphate show that this modification in the nitrite group arises from hydrogen-bonding with the electronegative phosphoryl-oxygen atom ($\equiv P \rightarrow \overset{\delta-}{O} \cdots \overset{\delta+}{H} \rightarrow \overset{\delta-}{O} = N = O$). The strength of the hydrogen-bonding in the complex is intermediate (Table 4) between that for water and for nitric acid in the phosphate; the shifts in ν_{OH} due to hydrogen-bonding ($\Delta\nu_{OH}$) from the values in the vapour state are regarded as a measure of the strength of the hydrogen bond and are proportional (Table 4) to the shifts in ν_{PO} ($\Delta\nu_{PO}$).

---

[1] Porter, *J. Chem. Phys.*, 1951, **19**, 1278.
[2] Bayliss and Watts, *Austral. J. Chem.*, 1956, **9**, 319.
[3] Hesford and McKay, *Trans. Faraday Soc.*, 1958, **54**, 573.
[4] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599.
[5] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.
[6] Penland, Lane, and Quagliano, *J. Amer. Chem. Soc.*, 1956, **78**, 887.

The frequency interval (Table 1) between the maxima of the ultraviolet absorption bands of the complex increases with increase in wavelength, as with the alkyl nitrites,[5] the average separation being 980 cm.$^{-1}$. For the alkyl nitrites[5] this frequency interval has been attributed to a vibrational transition of the excited state of the nitrite group as a whole, tending towards the structure $\mathrm{O{=\!=}N{=\!=}O}$ with fractional valencies. The prominence of the ultraviolet bands in Bu_3PO_4,HNO_2 supports this hypothesis since the hydrogen-bonding to P=O is able to modify the HNO_2 molecule towards $\mathrm{H{-}{-}{-}O{=\!=}N{=\!=}O}$. The ultraviolet absorption bands of the complex show evidence for slight asymmetry due, as for the alkyl nitrites, to superimposition of two band systems, namely, those for the *cis*- and the *trans*-isomer.

TABLE 4. *Variation of hydrogen bonding with* ν_{PO} *in tributyl phosphate complexes.*

	ν_{OH} for vapour	ν_{OH} for complex	ν_{PO} for complex	$\Delta\nu_{OH}/\Delta\nu_{PO}$ [a]
H_2O	3676 [b]	3450	1264	11·9
trans-HNO_2	3590 [c]	3060	1238	11·8
cis-HNO_2	3426 [c]	2735	1226	12·1
HNO_3	3560 [d]	2611 [e]	1208 [e]	12·6

[a] $\Delta\nu_{OH}$ is the difference between the value for the vapour and that when hydrogen-bonded to PO; $\Delta\nu_{PO}$ is the difference from that in tributyl phosphate (1283 cm.$^{-1}$). [b] Average of asymmetric and symmetric stretching frequencies for H_2O monomer; Thiel, Becker, and Pimentel, *J. Chem. Phys.*, 1957, **27**, 486. [c] Ref. 4. [d] Cohn, Ingold, and Poole, *J.*, 1952, 4272. [e] Nukada, Naito, and Maeda, *Bull. Chem. Soc. Japan*, 1960, **33**, 894.

The intensity of the ultraviolet bands, together with an almost quantitative extraction of nitrous acid by 100% tributyl phosphate, provides a sensitive method for the estimation[7] of aqueous nitrous acid at concentrations down to 10^{-4}M. Such determinations may require adjustment of the aqueous solutions to suitably dilute acid conditions, since (i) values of $q(HNO_2)$ fall in the presence of high concentrations of other acids which are extracted by the phosphates, *e.g.*, for 100% tributyl phosphate, from ~100 for $[HClO_4]_{org.} < 0{\cdot}1$M to 25 for $[HClO_4]_{org.} = 1{\cdot}2$M, and (ii) there is appreciable quenching of the ultraviolet absorption bands with high concentrations (>0·5M) of other acids in the organic phase.

The high extraction, by organic solvents containing donor oxygen groups, of nitrous acid, compared with that of other mineral acids [for 100% Bu_3PO_4 with <0·5M-acid in the aqueous phase; cf. $q(HNO_2) \sim 100$, with[8] $q(HF) = q(HClO_4) \sim 1$, $q(HNO_3) = q(HCl) = q(H_2SO_4) \sim 0{\cdot}01$] is largely a reflection of the ionisation of the other acids in the aqueous phase. Thus the value of the distribution coefficient for undissociated nitric acid, calculated after allowing for ionisation in the aqueous phase, is about 50 (for our conditions). For hydrofluoric acid, the relatively low value of q is attributed to stronger hydrogen-bonding in the aqueous phase.

EXPERIMENTAL

Solutions of nitrous acid in tributyl phosphate or tributyl phosphate–kerosene were prepared and examined at room temperature (~22°) by equilibration of the solvent with aqueous phases containing sodium nitrite in 10^{-2}M-sodium hydroxide to which perchloric or hydrochloric acid was added. Concentrated (0·5—1·0M) solutions for infrared examination were prepared by equilibration at 0°. Equilibrium between the phases was attained in less than 1 min.

Nitrous acid in the organic phases was determined by measuring the extinction coefficient at 391 mμ (Table 1).

Ultraviolet spectrophotometric measurements were made at room temperature with a Unicam S.P. 500 spectrophotometer, and infrared measurements at room temperature with a Hilger H-800 double-beam spectrometer equipped with a rock-salt prism. Samples for infrared examination were mounted as thin films ($\leqslant 2{\cdot}5 \times 10^{-3}$ cm.) between silver chloride windows.

The authors thank Mr. A. M. Deane for his advice during the infrared measurements.

CHEMISTRY DIVISION, A.E.R.E., HARWELL. [*Received, October 28th*, 1960.]

---

[7] Woodhead, U.K.A.E.A. Document A.E.R.E., R-3432, 1960.

[8] Hesford and McKay, *J. Inorg. Nuclear Chem.*, 1960, **13**, 156.