Studies in the Hydrolysis and Alcoholysis of Some Organic Nitrites.

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The kinetics and mechanisms of the hydrolysis of some simple organic nitrites were investigated, and the products of alcoholysis determined in some cases. The acid-catalysed hydrolysis of *n*-propyl, *tert.*-butyl, and diphenylmethyl nitrites has been studied at 0° in 72·5% (w/w) dioxan–water. In very dilute acid solution containing halide ions, the overall equation $-d[RO{\cdot}NO]/dt = k_2[H^+][RO{\cdot}NO] + k_3[H^+][RO{\cdot}NO][Halide^-]$ holds. The position of equilibrium between alkyl nitrite, water, nitrous acid, and the alcohol has been determined for *n*-propyl and *tert.*-butyl nitrites. A volumetric method for the determination of the total hydrolysable nitrous acid content of these esters is described. The alkaline hydrolysis of *n*-propyl and *tert.*-butyl nitrites has been studied in aqueous dioxan between 25° and 55°. The reactions are of the second order, but with *n*-propyl nitrite a small solvolytic component is indicated. Arrhenius parameters are given.

Except in the alcoholysis of triphenylmethyl nitrite, which leads to formation of the ether, nitrosyl–oxygen bond fission was found in all cases as is shown by retention of configuration during hydrolysis of optically-active 1-methylheptyl nitrite, by the alcoholysis products of *n*-propyl and *tert.*-butyl nitrites, and, for the *tert.*-butyl ester in acid solution, by the absence of olefin formation and by experiments with isotopically enriched water.

The results are interpreted in terms of the probable reaction mechanisms.

The investigations carried out here into the mechanisms of reactions of organic esters (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603; Day and Ingold, *ibid.*, p. 686) have been extended to some simple organic nitrites. Fischer (*Z. physikal. Chem.*, 1908, **65**, 61) considered that the acid-catalysed hydrolysis of ethyl nitrite was too rapid at room temperature to be measured by conventional methods. Skrabal, Zahorka, and Wiemann (*ibid.*, 1939, *A*, **183**, 345) found that the rate of hydrolysis in slightly acid solutions containing acetate buffers increased slightly with methylation of the α-carbon atom in the series methyl—*tert.*-butyl nitrite. In alkaline solution the rates of hydrolysis were very much slower, but consistent results could not be obtained.

Acid Catalysis.—(i) n-*Propyl nitrite.* The hydrolysis of *n*-propyl nitrite has been studied at 0° in 72·5% (w/w) dioxan–water in the presence of small concentrations of mineral acids and their salts. The overall reaction is

$$Pr^nO{\cdot}NO + H_2O \overset{H^+}{\rightleftharpoons} Pr^n{\cdot}OH + HO{\cdot}NO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (A)$$

The position of equilibrium for this reaction was determined at 0° in various dioxan–water mixtures. Values for the concentration equilibrium constant $K = [ROH][HO{\cdot}NO]/[RO{\cdot}NO][HOH]$ were obtained for a wide range of initial concentrations giving a mean value of $K = 15{\cdot}7 \times 10^{-3}$. Individual results varied from 11·3 to $18{\cdot}6 \times 10^{-3}$.

With perchloric acid (0·001—0·007M) the observed first-order rate coefficients were found to be proportional to the hydrogen-ion concentration, the rate expression being:

$$-d[RO{\cdot}NO]/dt = k_1[RO{\cdot}NO] = k_2[H^+][RO{\cdot}NO] \quad . \; . \; . \; . \; . \; . \quad (B)$$

First-order kinetics are observed in any one run, since the hydrogen-ion concentration is virtually unaffected by the weakly ionised nitrous acid released on hydrolysis. Since water is in large excess, its active mass is also constant, and is incorporated in k_1 and k_2.

In the presence of hydrochloric acid a faster rate of hydrolysis was observed than with equivalent concentrations of perchloric acid. The rate was no longer directly proportional to the acid concentration, but could be expressed by the equation:

$$-\mathrm{d}[\mathrm{RO{\cdot}NO}]/\mathrm{d}t = k_2[\mathrm{HCl}][\mathrm{RO{\cdot}NO}] + k_3[\mathrm{HCl}]^2[\mathrm{RO{\cdot}NO}] \quad . \; . \; . \; . \; . \quad (C)$$

Since hydrochloric acid is a strong acid under these conditions, the hydrogen-ion and chloride-ion concentrations may be equated to that of the acid added, and equation (*C*) may be written:

$$-\mathrm{d}[\mathrm{RO{\cdot}NO}]/\mathrm{d}t = k_2[\mathrm{H^+}][\mathrm{RO{\cdot}NO}] + k_3[\mathrm{H^+}][\mathrm{Cl^-}][\mathrm{RO{\cdot}NO}] \quad . \; . \; . \; . \; . \quad (D)$$

Table 1 shows the first-order rate constants for this ester at varying concentrations of the two acids. The results with perchloric acid give, for hydrogen-ion catalysis, a mean value of $k_2 = 0{\cdot}219$ sec.$^{-1}$ mole^{-1} l. This value is used in the interpretation of the results with hydrochloric acid, which give, for chloride-ion catalysis, a value of $k_3 =$ 39 sec.$^{-1}$ mole^{-2} l.^{2}.

TABLE 1. n-*Propyl nitrite; acid catalysis.*

Temp. 0°. Solvent 72·5% dioxan–water.

$10^3[\mathrm{HClO_4}]$, M	6·60	4·80	3·40	2·25	1·70	1·02	
$10^4 k_1$, sec.$^{-1}$	14·3	10·4	7·55	4·94	3·70	2·26	
k_2, sec.$^{-1}$ mole^{-1} l.	0·217	0·217	0·222	0·220	0·218	0·222	
$10^3[\mathrm{HCl}]$, M	3·90	3·40	3·00	2·62	1·90	1·42	0·70
$10^4 k_1$, sec.$^{-1}$	13·9	11·35	9·95	8·35	5·75	4·18	1·84
k_3, sec.$^{-1}$ mole^{-2} l.^{2}	34·2	33·8	37·0	37·0	43·1	44·6	42·2

Consistently, the addition of sodium bromide to solutions of fixed hydrogen-ion (perchloric acid) concentration, and sufficient sodium perchlorate to maintain constant ionic strength, produced an increase in rate proportional to the concentration of added halide ions. This is in accordance with equation (*D*) when the first term is constant and only the halide ion varies in the second term. The results obtained were as follows:

n-*Propyl nitrite; bromide-ion catalysis.*

Temp. 0°. Solvent 72·5% dioxan–water. $[\mathrm{HClO_4}] = 0{\cdot}0024$M.

$10^3[\mathrm{NaBr}]$, M	11·6	10·2	6·60	4·40	2·40	0
$10^4 k_1$, sec.$^{-1}$	13·0	12·3	9·64	8·52	7·02	5·49
k_3, sec.$^{-1}$ mole^{-2} l.^{2}	26·9	27·7	26·2	28·5	26·5	—

(ii) tert.-*Butyl nitrite.* The same conditions were used for the investigation of the acid-catalysed hydrolysis of this ester. Catalysis by hydrogen ions (perchloric acid) was found to be some 2—3 times greater, whilst catalysis by bromide ions was much less marked than with *n*-propyl nitrite. In both cases the catalysis was proportional to the concentrations of the respective ions. With this ester a small increase in rate was observed on addition of sodium perchlorate. Equilibrium determinations indicated that the hydrolysis is virtually complete under the conditions used for the kinetic studies. Table 2 shows the results obtained.

TABLE 2. tert.-*Butyl nitrites; acid catalysis.*

(a) *Perchloric acid.*

$10^3[\mathrm{HClO_4}]$, M	3·70	2·96	2·34	2·22	1·78	1·48	1·21	0·74
$10^4 k_1$, sec.$^{-1}$	19·4	15·5	12·0	11·3	9·02	7·55	6·04	3·67
k_2, sec.$^{-1}$ mole^{-1} l.	0·524	0·523	0·513	0·510	0·507	0·511	0·500	0·496

(b) *Sodium bromide.* $[\mathrm{HClO_4}] = 0{\cdot}00234$M.

$10^3[\mathrm{NaBr}]$, M	11·7	9·30	6·80	5·00	2·50	0
$10^4 k_1$, sec.$^{-1}$	16·1	15·9	15·2	14·7	14·3	13·8
k_3, sec.$^{-1}$ mole^{-2} l.^{2}	8·4	9·6	8·8	7·7	8·5	—

(iii) *Diphenylmethyl nitrite.* A limited investigation was carried out on a small quantity of diphenylmethyl nitrite, to determine the order of magnitude of the catalytic constants. For hydrogen-ion catalysis, $k_2 = 0{\cdot}19$ sec.$^{-1}$ mole^{-1} l. and for bromide ions,

$k_3 = 27$ sec.$^{-1}$ mole^{-2} l.^{2}. These values are only approximate, since it was not practicable to purify the ester completely.

(iv) *Position of bond fission.* (—)-1-Methylheptyl nitrite was prepared by the action of nitrosyl chloride on (—)-octan-2-ol in pyridine. Since it is difficult to formulate a mechanism which would disturb the asymmetric centre, it is assumed that the configuration is retained, and thus the optical rotations of the two compounds with the same configuration are obtained. The optical course of the hydrolysis of this ester in acidic aqueous dioxan corresponded to complete retention of configuration. This implies fission of the nitrosyl-oxygen bond $RO\!:\!{-}{-}{-}NO$. The reverse reaction, between nitrous acid and (+)-octan-2-ol in water at 0°, produced (+)-1-methylheptyl nitrite in good yield without racemisation, showing that the reaction proceeds by nitrosation of the oxygen atom of the alcohol.

Bond-fission experiments with *tert.*-butyl nitrite were carried out by two methods. First an attempt was made to detect any small amounts of olefin which would inevitably be formed if any part of the acid-catalysed hydrolysis proceeded by a unimolecular alkyl-oxygen fission mechanism. No olefin could be detected by methods sensitive to as little as 0·1% of this product. The acid-catalysed hydrolysis was next carried out in the presence of water enriched with $H_2{}^{18}O$, supplied by Dr. D. R. Llewellyn of this Department. Any uni- or bi-molecular alkyl-oxygen fission would yield *tert.*-butanol containing an increased proportion of ^{18}O. The alcohol was separated by azeotropic distillation with benzene, and the isotopic composition of the water formed on pyrolysis was determined by Dr. C. A. Bunton, using the mass spectrometer. The ^{18}O content was normal. These two experiments show clearly that the hydrolysis of *tert.*-butyl nitrite under the conditions used proceeds exclusively by nitrosyl-oxygen fission, from which it is concluded that alkyl-oxygen fission is extremely unlikely in the hydrolysis of any simple alkyl nitrite under similar conditions.

The Mechanism of Acid-catalysed Hydrolysis.—The following mechanistic interpretations are consistent with our observations:

(1)	$RO{\cdot}NO + H^+$	$\rightleftharpoons$	$(RO{\cdot}NOH)^+$	Fast proton transfer
(2*a*)	$(RO{\cdot}NOH)^+$	$\rightleftharpoons$	$ROH + NO^+$	Unimolecular heterolysis
(2*b*)	$(RO{\cdot}NOH)^+ + HOH$	$\rightleftharpoons$	$ROH + (HO{\cdot}NOH)^+$	Bimolecular solvolysis
(2*c*)	$(RO{\cdot}NOH)^+ + X^-$	$\rightleftharpoons$	$ROH + NOX$	Bimolecular attack by halide ion
(3*a*)	$NO^+ + HOH$	$\rightleftharpoons$	$(HO{\cdot}NOH)^+$	Removal of products
(3*c*)	$NOX + HOH$	$\rightleftharpoons$	$HO{\cdot}NO + H^+ + X^-$	
(4)	$(HO{\cdot}NOH)^+$	$\rightleftharpoons$	$HO{\cdot}NO + H^+$	Fast proton transfer

It is considered that the equilibria (1) and (4) are established rapidly, and are maintained throughout the reaction. Since the forward velocities of the rate-determining steps (2*a*), (2*b*), and (2*c*) are proportional to the concentration of the protonated ester, the position of equilibrium (1) for the different esters is probably a major factor in the observed variations in the rates of hydrolysis. It is also possible that the rapidity of the acid-catalysed hydrolysis of these esters, as compared with the much slower reactions of the simple carboxylic esters, may also be due largely to differences in the equilibrium concentrations of the protonated species.

There are three possible rate-determining steps. From the present results no definite distinction may be drawn between steps (2*a*) and (2*b*), since the kinetic forms of both are the same in aqueous solvents. However, the sensitivity of the reaction to small concentrations of halide ions indicates that attack by nucleophilic reagents takes place readily, and it therefore seems that the more probable mechanism involves the bimolecular attack by a water molecule, as in (2*b*). When halide ions are present in aqueous solution, the reactions (2*b*) and (2*c*) occur simultaneously, giving rise to the observed rate equation (*D*). The catalysis by halide ions, resulting in the intermediate formation of the nitrosyl halide, is analogous to the halide-ion catalysis of the rate of diazotisation of amines with acidified nitrous acid solutions (Schmid, *Z. Elektrochem.*, 1936, **42**, 579). The high reactivity of the protonated esters towards relatively weak nucelophilic reagents (water, halide ions), in contrast to the slow reaction of the esters, even with the strongly nucleophilic hydroxide ion, is also paralleled by the very great difference between the nitrosating power of the nitrous acidium ion $(HO{\cdot}NOH)^+$ and nitrous acid. Whereas the diazotisation of *o*-chloroaniline by the nitrous acidium ion proceeds rapidly in dilute solutions at 0°, the reaction with nitrous acid under similar conditions is undetectable (Ingold, *Bull. Soc. chim*. 1952, 667).

Alkaline Hydrolysis.—The hydrolysis of *n*-propyl and *tert.*-butyl nitrites has been studied in aqueous dioxan solutions in the presence of varying dilute concentrations of sodium hydroxide. The rate of disappearance of alkali was measured over the temperature range 25—55°. Under comparable conditions at 35° *tert.*-butyl nitrite is hydrolysed some 50 times more slowly than *n*-propyl nitrite, and owing to thermal decomposition of the former ester only the early stages of the hydrolysis could be followed accurately. Good second-order kinetics were observed in all cases, and the rate coefficients were in accordance with the relation: $\log_{10} k = \log_{10} A - E/(2{\cdot}303\boldsymbol{R}T)$). Table 3 shows the results, together with the values of $\log_{10} A$ and E calculated from the Arrhenius equation.

TABLE 3. *Alkaline hydrolysis.*

Solvent, wt. % of dioxan	Ester	Initial [RO·NO], M	Initial [NaOH], M	$10^6 k_2$, sec.$^{-1}$ mole^{-1} l. at 25·1°	35·1°	45·0°	55·1°	$\log_{10} A$	E, kcal.
72·5	Pr^n	0·025	0·054	26·5	81·6	185	465	9·17	18·7
60	,,	0·03	0·054	30·4	76·2	181	—	8·31	17·5
60	Bu^t	0·025	0·15	0·55	1·37	3·83	10·6	8·33	20·0
60	,,	0·12	0·15	0·43	1·27	3·71	—	9·22	21·3

With *n*-propyl nitrite the rate of hydrolysis over a wider range of initial concentrations of sodium hydroxide was investigated at 35° in 60% dioxan–water, and the following second-order rate coefficients were obtained:

Initial [NaOH,] M	0·055	0·114	0·115 (+0·117M-NaCl)	0·167
$10^6 k_2$	75·5	67·8	64·0	58·1

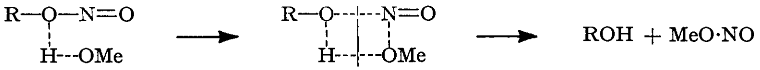
Their decrease with increasing concentration of alkali may be attributed to an ionic strength effect, and/or to an underlying solvolytic reaction. The smaller decrease when sodium chloride is added shows that only a small part of the variation can be due solely to changing ionic strength. The instantaneous rate coefficients, $(1/[\mathrm{RO{\cdot}NO}])\, d[\mathrm{RO{\cdot}NO}]/dt = k_1 + k_2[\mathrm{OH}^-]$, were plotted against hydroxide concentration. The slope of the straight line obtained gave a corrected value for $k_2 = 50{\cdot}5 \times 10^{-6}$ sec.$^{-1}$ mole^{-1} l., and the intercept gave $k_1 = 1{\cdot}5 \times 10^{-6}$ sec.$^{-1}$. Part of this value of k_1 is due to the ionic strength effect, and it should, therefore, be regarded as a maximum value for the solvolytic component of the reaction.

The position of bond fission under alkaline conditions was determined by following the optical course of the hydrolysis of (+)-1-methylheptyl nitrite in dilute alkaline aqueous ethyl alcohol. The configuration was retained, as found for the hydrolysis of 1-methylbutyl nitrite with concentrated alcoholic potash (Hoye, Ph.D. Thesis, London, 1953). It may, therefore, be concluded that the alkyl–oxygen bond of these esters remains intact during the reaction. Since the unimolecular heterolysis of the nitrosyl–oxygen bond is even less likely to occur in alkaline than in acid solution (Day and Ingold, *loc. cit.*, p. 702), it seems most probable that the alkaline hydrolysis proceeds by the nucleophilic attack of a hydroxide ion on the nitrogen atom of the ester.

Alcoholysis Reactions.—Kenyon and Young (*J.*, 1938, 965) have shown that the neutral alcoholysis of (—)-1-methylheptyl nitrite with *sec.*-butyl alcohol produces (—)-octan-2-ol. Since the occurrence of a small proportion of alkyl–oxygen fission might not have been detectable in this reaction, experiments were carried out in which *n*-propyl and *tert.*-butyl nitrites were separately dissolved in their respective alcohols, and sealed in dark glass containers at 35°. The formation of ethers by alkyl–oxygen bond fission is irreversible, so even a small amount of this mechanism would result in a gradual accumulation of the ether. On analysis after six weeks, no significant amount of the ether was detected in either mixture.

The occurrence of alkyl–oxygen fission was finally observed in the neutral alcoholysis of triphenylmethyl nitrite. The ester could not be isolated pure, owing to its very rapid decomposition at room temperature, and the specimen used was a pasty yellow solid suspended in a small amount of dry ether. It reacted with dry methyl alcohol rapidly at room temperature, and the methyl nitrite formed was removed immediately by evaporation under reduced pressure: this procedure ensures that the products closely approximate to the true proportion of alkyl- to nitrosyl-oxygen bond fission. The methyl ether of triphenylmethyl alcohol was formed in good yield. Similar experiments with *n*-propyl alcohol gave the *n*-propyl ether as the sole product.

The comparative ease with which the simple alkyl nitrites react with methyl alcohol to give methyl nitrite must be reconciled with the very slow rate of hydrolysis in aqueous alkali. Neither a unimolecular process nor a simple nucleophilic attack by an alcohol molecule would be sufficiently rapid to account for the ester exchange reaction. A possible explanation may be that the initial step consists of the formation of a hydrogen bond between the solvent molecule and the ester, followed by a nucleophilic attack on the nitrogen atom:



$$\begin{array}{l} \mathrm{R{-}O{-}N{=}O} \\ \;\;\vdots \\ \mathrm{H{\cdots}OMe} \end{array} \longrightarrow \begin{array}{l} \mathrm{R{-}O{\cdots}|{\cdots}N{=}O} \\ \;\;\vdots\quad|\quad\vdots \\ \mathrm{H{\cdots}|{\cdots}OMe} \end{array} \longrightarrow \mathrm{ROH + MeO{\cdot}NO}$$

The partial (or complete) transfer of a proton would increase the nucleophilic power of the alcohol molecule, and would also increase the susceptibility of the nitrogen atom to attack. The second stage would, therefore, be greatly facilitated. A comparative kinetic investigation with various nitrous esters would help to clarify this problem.

EXPERIMENTAL

Materials.—Dioxan was purified and dried by Vogel's method ("Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 175). *n*-Propyl and *tert.*-butyl nitrites were prepare in aqueous solution by Noyes's method (*Org. Synth.*, 1936, **16**, 7). They were distilled through a 12″ helix-packed column under reduced pressure, and had b. p. 48·5°/760 mm., n_{D}^{20} 1·3605, n_{D}^{25} 1·3578 (Cowley and Partington, *J.*, 1933, 1252); and b. p. 63·5°/760 mm., n_{D}^{20} 1·3687, n_{D}^{25} 1·3660 (Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516). Octan-2-ol was resolved into its optical isomers by Kenyon's phthalic anhydride–brucine method (see Vogel, *op. cit.*, p. 489), giving (−)-octan-2-ol, b. p. 80°/15 mm., $[\alpha]_{\mathrm{D}}^{18}$ −9·75°, and (+)-octan-2-ol, b. p. 80°/15 mm., $[\alpha]_{\mathrm{D}}^{18}$ +9·41°. From the (+)-alcohol obtained, (+)-1-methylheptyl nitrite was prepared by the aqueous method of Noyes (*op. cit.*), giving b. p. 63—64°/15 mm., $[\alpha]_{\mathrm{D}}^{18}$ +5·11°. (−)-1-Methylheptyl nitrite was prepared by the action of nitrosyl chloride on the (−)-alcohol in pyridine (Kenyon and Young, *loc. cit.*); it had b. p. 63—64°/15 mm., $[\alpha]_{\mathrm{D}}^{18}$ −5·26°. Attempts to prepare diphenylmethyl nitrite and triphenylmethyl nitrite by this method failed: it was therefore modified by using exactly equimolecular quantities of the alcohol and pyridine in dry ether, and continuing the addition of nitrosyl chloride until a slight excess had been added. The pyridine hydrochloride was filtered off, and the ether removed by evaporation under reduced pressure. With diphenylmethyl nitrite a yellow liquid was obtained, which decomposed on distillation, even at 65°/0·1 mm. This product, which was used for the kinetic investigation, contained 81% of hydrolysable nitrous acid (Found: C, 75·4; H, 5·5%. This composition would be given approximately by a mixture of 80% diphenylmethyl nitrite and 20% diphenylmethyl alcohol). The triphenylmethyl nitrite so prepared was a pasty yellow solid which decomposed rapidly, becoming dark brown and evolving copious nitrous fumes, when the last traces of ether were removed. For the investigation of the products of alcoholysis, the crude preparation was used immediately without removing the last few ml. of ether.

Acid Hydrolysis.—Solutions were made up by weight from dioxan, carbon dioxide-free distilled water, and standard solutions of the acids and salts. The reaction flask was fitted with a jacketed automatic pipette, which was kept at the reaction temperature by circulating water from the ice-water thermostat. The appropriate ester (0·7—1 ml.) was added, and samples (7·80 ml.) of the solution were removed at intervals of 1—2 min., depending on the speed of the reaction, run into stoppered flasks containing carbon tetrachloride (35 ml.) and dilute sodium hydroxide (13 ml.; excess) at 0°, and titrated later with approximately 0·01N-hydrochloric acid, 9 : 2 neutral red–bromothymol blue being used as mixed indicator. The following are details of two typical rate measurements in 72·5% dioxan–water at 0° :

(*a*) n-*Propyl nitrite* (perchloric acid = 0·0048N).

Time (min.)	0	2	3·5	5	6·5	8	9·5	11	12·5	∞
Titre (ml. HCl)	24·60	21·55	19·27	17·33	15·84	14·33	13·81	11·98	10·50	−1·80
$\log_{10}$ (titre–titre $_\infty$) ...	1·422	1·368	1·324	1·282	1·247	1·208	1·165	1·139	1·090	—

The " infinity " titre is corrected to allow for the position of equilibrium under these conditions. The first-order rate coefficient, obtained from the graph of $\log_{10}$ (titre–titre $_\infty$) against time, is $k_1 = 10{\cdot}4 \times 10^{-4}$ sec.$^{-1}$.

(*b*) tert.-*Butyl nitrite* (perchloric acid = 0·0023N).

Time (min.)	0	2	3	4	5	6	7	8	9	∞
Titre (ml. HCl)	28·59	25·55	23·94	22·64	21·42	20·26	19·21	18·16	17·17	4·94
$\log_{10}$ (titre–titre $_\infty$) ...	1·373	1·314	1·279	1·248	1·217	1·185	1·154	1·121	1·087	—

The hydrolysis of this ester is complete (>99%) at equilibrium. These measurements give $k_1 = 12{\cdot}0 \times 10^{-4}$ sec.$^{-1}$.

Equilibrium Measurements.—Samples of the esters (0·4—1·7 g.) were weighed in small glass ampoules, which were crushed under dioxan–water solutions at 0° containing varying amounts of hydrochloric acid. In some cases the corresponding alcohol was also added. After about 20 half-lives of the hydrolysis samples were withdrawn and the free nitrous acid determined as described above. The total hydrolysable nitrous acid contained by the esters was determined by oxidation with ceric sulphate solution. Since the nitrous acid is removed the hydrolysis goes to completion, and the excess of ceric ion may be determined iodometrically. By this method, the samples of *n*-propyl nitrite used were found to contain 99% of the theoretical amount of nitrous acid, but the figure for *tert.*-butyl nitrite, even though freshly prepared, could not be increased above 96·8%.

Bond Fission.—(i) *Optical methods.* (−)-1-Methylheptyl nitrite, $[\alpha]^{18}_{D}$ −5·26° (2 ml.), was dissolved in dioxan (50 ml.) and water (5 ml.), and one drop of concentrated hydrochloric acid was added after the initial rotation had been measured; $[\alpha]^{18}_{D}$ −0·25° (*l*, 1) ⟶ −0·44° (3 days) ⟶ −0·46° (final, 5 days). The alkaline solution used contained sodium hydroxide (2 g.) in water (5 ml.) and ethanol (50 ml.). The (+)-1-methylheptyl nitrite, $[\alpha]^{18}_{D}$ +5·05° (4 ml.), was added, giving an initial rotation, α^{18}_{D} +0·40° (*l*, 1). During 7 days the rotation of the solution increased steadily, reaching a maximum of +0·68°.

(ii) *Olefin determinations.* The reaction mixture was dioxan-water (72·5%; 200 ml.), containing 0·01M-hydrochloric acid at 0°. The system was thoroughly swept out with nitrogen, and, with a slow stream of nitrogen passing continuously, *tert.*-butyl nitrite (5 ml.) was added. The exit gases passed through 20% sodium hydroxide solution, over solid potassium hydroxide, solid calcium chloride, and through *n*-heptane at −80°. After 20 min. the temperature of the reaction mixture was raised slowly to 45° and kept there for 30 min. to decompose all the nitrous acid. After the flask had cooled to 0° the heptane trap was removed and treated with bromine in carbon tetrachloride. The excess of bromine was titrated, potassium iodide and sodium thiosulphate being used [Found : Bromine remaining equivalent to (*a*) 25·35 ml., (*b*) 25·38 ml. of thiosulphate. Total bromine added = 25·37 ml. of thiosulphate].

(iii) *Acid hydrolysis with* $H_2{}^{18}O$. The reaction mixture was a mixture of dioxan (145 g.) and water (54 ml.) containing excess of ^{18}O. " AnalaR " 70% perchloric acid was added (0·2 ml.), and the mixture cooled to 0°. *tert.*-Butyl nitrite (10 ml.) was added, and after 20 min. the aqueous and the organic liquid were separated by the addition of dry sodium chloride (15 g.). The aqueous layer was extracted with dry ether, and the organic layer and ether washings together were neutralised and dried (K_2CO_3, followed by $CaSO_4$). Dry benzene (100 ml.) was added, and the mixture fractionated through a 36″ helix-packed electrically heated column. The *tert.*-butanol–benzene azeotrope (Young, *J.*, 1902, 746) was obtained, b. p. 73·1/760 mm., $n^{24\cdot8}_{D}$ 1·4490—1·4491 (C, 81·1; H, 10·35%). To check the identity of this product, a mixture of 60 g. of redistilled, dried " AnalaR " benzene and 40 g. of redistilled, lithium-dried *tert.*-butanol was fractionated. The azeotrope obtained had b. p. 73·1°/760 mm., $n^{24\cdot8}_{D}$ 1·4490 (Found : C, 81·5; H, 10·1%). Samples of the azeotrope from the hydrolysis were pyrolysed at 500° for 24 hr. : the products were condensed at −80°, and any volatile matter pumped off at that temperature. About 10 mm. of carbon dioxide was added and the tube resealed. After equilibrium had been established between the carbon dioxide and the water produced by the pyrolysis (Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, **60**, 679) the ^{18}O content of the carbon dioxide was measured in the mass spectrometer by Dr. Bunton, and compared with samples of the same carbon dioxide which had been allowed to come to equilibrium with normal water. By using the formula: Total atom $\%^{18}O = 100/(2{\cdot}076R + 1)$, where R is the ratio of carbon dioxide of mass 44 : mass 46, the following results were obtained :

Source	Excess, atom %, of ^{18}O (over normal water) (1)	(2)
$H_2{}^{18}O$ water used	1·930	2·900
tert.-Butanol from hydrolysis	0·001	−0·002

Alkaline Hydrolysis.—Solutions were made up at room temperature from dioxan, carbon dioxide-free distilled water, " AnalaR " sodium hydroxide, and the appropriate ester. Equal samples (7·00 ml.) were sealed in hard-glass tubes and placed in thermostats. At appropriate times tubes were removed, cooled to 0°, crushed under carbon tetrachloride at 0°, and titrated as described earlier. " Infinity " values were found by crushing tubes under dioxan–water solutions containing a known excess of hydrochloric acid at 0°, and later titrating the total acid produced, making allowance for the position of equilibrium. Typical measurements, one for each ester, carried out at 35·1° in 60% (by weight) dioxan–water are given :

(*a*) n-*Propyl nitrite.*

Time (hr.)	0	17	24	40	51	68	94	164	185	∞
10^2[NaOH], M	5·44	4·81	4·60	4·26	4·06	3·82	3·50	3·05	2·97	2·52
10^6k_2 (sec.$^{-1}$ mole^{-1} l.)	—	78·5	83·5	76·5	72·5	75·0	78·0	78·0	78·0	—

(*b*) tert.-*Butyl nitrite.*

Time (hr.)	0	42	67	86	114	150	182	∞
10^2[NaOH], M	15·72	15·64	15·59	15·56	15·50	15·45	15·40	13·26
10^6k_2 (sec.$^{-1}$ mole^{-1} l.)	—	1·38	1·39	1·39	1·46	1·39	1·37	—

Alcoholyses.—*n*-Propyl nitrite (62 ml.) and dry *n*-propyl alcohol (120 ml.) were sealed in a dark-glass flask, and kept at 35° for 6 weeks. The ester was distilled off and the residue extracted with water and ether. The ether extract was dried and distilled, leaving a residue (3·5 ml.), b. p. >50°. This was extracted with water (20 ml.), and the remaining organic liquid (1·5 ml.) was distilled from sodium giving a liquid (1 ml.), b. p. 88°, n_D^{20} 1·3818 (cf. *n*-propyl alcohol, b. p. 97°, n_D^{20} 1·3833, and di-*n*-propyl ether, b. p. 90°, n_D^{20} 1·3809). *tert.*-Butyl nitrite (60 ml.) and dry *tert.*-butyl alcohol (120 ml.) were mixed and treated as above. About 0·5 ml. of residue was obtained, which reacted completely with sodium metal, giving a negligible distillate.

Dry methyl alcohol (50 ml.) was added to triphenylmethyl nitrite suspension in dry ether (6 ml.). The solution was evaporated rapidly under reduced pressure, while the temperature was raised to 35°. Successive crystalline fractions were obtained; the three major fractions (3·3 g.) had m. p. 82—83°, leaving a residue (0·3 g.), m. p. 100—120° (Found, for the second fraction : C, 88·2; H, 6·5. Calc. for methyl triphenylmethyl ether: C, 87·6; H, 6·6%). A control experiment with triphenylmethyl alcohol in dry methyl alcohol gave only triphenylmethyl alcohol, m. p. 161°. A second portion (6 ml.) of the ester in ether was added to dry *n*-propyl alcohol (50 ml.), and kept at room temperature for 48 hr. The solution was evaporated at reduced pressure, leaving 5 ml. of a yellow oil which was recrystallised with difficulty from methyl alcohol and water. Pale yellow crystals (3·9 g.) were obtained, m. p. 55° (Found : C, 87·1; H, 7·3. Calc. for *n*-propyl triphenylmethyl ether : C, 87·3; H, 7·3%).

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