Esters of Inorganic Oxyacids. Part I. The Mechanism of Hydrolysis of Alkyl Esters, ^{18}O *being used as Tracer, and its Relation to other Reactions in Alkaline Media.*

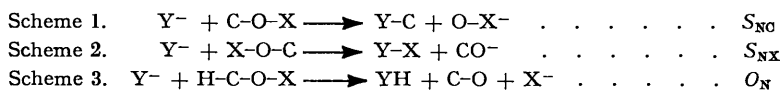By M. Anbar, I. Dostrovsky, David Samuel, and A. D. Yoffe.

The mode of bond fission in the alkaline hydrolysis of a number of esters of inorganic oxyacids has been determined by using ^{18}O-labelled compounds. These include esters of hypochlorous, hypobromous, chloric, bromic, iodic, perchloric, sulphuric, nitrous, nitric, and chromic acid, and also acetic acid. Of the esters studied, only triphenylmethyl perchlorate, sulphate, and nitrate and *tert.*-butyl nitrate are hydrolysed with alkyl–oxygen fission. *n*-Butyl and *n*-octyl nitrates, triphenylmethyl chromate and acetate, and diethyl sulphate are hydrolysed only partly by alkyl–oxygen fission, and the remainder retain the alkyl–oxygen bond in hydrolysis.

The mode of bond fission occurring in the alkaline hydrolysis is discussed in relation to the strength of the acid and the nature of the alkyl group. The relationship of other reactions of these esters, such as alkylation, halogenation, nitration, nitrosation, and oxidation, is discussed.

Esters of inorganic oxyacids offer an interesting series for the study of the properties of the C–O–X bonds, where X is the central atom of an oxyacid, and for correlation of the reactions of such esters with the electronegative character of the inorganic acid residue. Many of these esters are used as reagents in organic chemistry (*viz.*, hypochlorites, chromates, nitrites, nitrates, and sulphates). A comparison of such reactions with hydrolysis, on the one hand, and with the properties of the acid and alkyl components of the ester, on the other, may help in unifying and interpreting the various known reactions and in predicting possible new reactions and reagents.

Kinetic measurements for some of these esters have already been reported. *tert.*-Butyl, propyl, and diphenylmethyl nitrites have been studied by Allen (*Nature*, 1953, **172**, 301) who demonstrated that their alkaline hydrolysis proceeds by a nucleophilic attack on nitrogen. Hammett and Lucas (*J. Amer. Chem. Soc.*, 1942, **64**, 1928) have reported the rates of alkaline hydrolysis of *tert.*-butyl and benzyl nitrates. Baker and Easty (*J.*, 1952, 1193, 1208) made an extensive study of the alkaline hydrolysis of methyl, ethyl, *iso*propyl, and *tert.*-butyl nitrates, and showed that the hydrolysis of the *tert.*-butyl ester proceeds by an S_N1 mechanism whereas methyl and ethyl nitrates are hydrolysed by an S_N2 mechanism. They also found that parallel reactions lead to the formation of olefins and oxidation products. In connection with their studies of the mechanism of chromate oxidation, Leo and Westheimer (*J. Amer. Chem. Soc.*, 1952, **74**, 4383) have shown that the rates of hydrolysis of *iso*propyl and *tert.*-butyl chromates are base-catalysed. The kinetics of the formation and hydrolysis of *tert.*-butyl hypochlorite have been investigated in both alkaline and acid media by Anbar and Dostrovsky (*J.*, 1954, 1094). In the alkaline hydrolysis the reaction proceeds by nucleophilic attack on chlorine. The hydrolysis of triphenylmethyl perchlorate has been reported as being both acid- and base-catalysed (Bodforss and Ahrland, *Acta Chem. Scand.*, 1951, **5**, 227).

It appears from the kinetic work summarised above and from general considerations that nucleophilic attack on compounds of the general type C–O–X may occur in several ways : (*a*) A nucleophilic attack of the reagent Y on the α-carbon atom of the alkyl group, denoted by the symbol S_{NC}.* (*b*) A nucleophilic attack of Y on the central atom X of the oxyacid, denoted by S_{NX}. (*c*) An oxidation reaction, similar to the well-known nucleophilic elimination reactions, denoted by O_N. In this case the hydrogen atom attached to the α-carbon atom of the alkyl group is removed by the reagent Y and the group X is detached as an anion, with the formation of a double bond between carbon and oxygen. Each of these schemes may of course proceed by either a bimolecular or a unimolecular mechanism, though not all of the various possibilities have been observed. These schemes are summarised below :

Scheme 1. $Y^- + C\text{-}O\text{-}X \longrightarrow Y\text{-}C + O\text{-}X^-$ . . . . . . S_{NC}

Scheme 2. $Y^- + X\text{-}O\text{-}C \longrightarrow Y\text{-}X + CO^-$ . . . . . . S_{NX}

Scheme 3. $Y^- + H\text{-}C\text{-}O\text{-}X \longrightarrow YH + C\text{-}O + X^-$ . . . . . . O_N

Point of Bond Fission.—In order to distinguish between schemes 1 and 2, the alkaline hydrolysis of a number of esters of inorganic acids was studied, by using water enriched with respect to ^{18}O. In some cases the results were checked by repeating the experiments, esters labelled with ^{18}O in the alkoxy-group and normal water being used.

Many of these esters were synthesised by standard methods (see Experimental section). The hypochlorite, chlorate, bromate, and iodate of triphenylmethanol have not been prepared before (cf. unsuccessful attempts to prepare chlorites, Levi, *Gazzetta*, 1923, **53**, 40). Attempts to prepare esters of permanganic and cyanic acids were unfortunately unsuccessful.

This paper deals in general with tertiary esters of monobasic oxyacids, although a certain number of other esters have been included. These experiments are now being extended to esters of polybasic acids.

The alcohols resulting from each experiment were isolated, purified, and subjected to isotopic analysis. The type of bond fission occurring is indicated in Table 1.

Kinetic studies have shown that a change in the nature of the alkyl group may cause a change in the order of the reaction from bimolecular to unimolecular $S_N2 \longrightarrow S_N1$ (Ingold, "Structure and Mechanism in Organic Chemistry," 1953, Cornell Univ. Press, p. 316). Similarly, in the alkaline hydrolysis of esters of oxyacids we have found that such a change may also alter the point of attack, *i.e.*, from S_{NC} to S_{NX} (cf. Table 1). However, the change in order of the reaction is more sensitive to the nature of the alkyl group. For instance, in the series : phenyl, *n*-alkyl, *sec.*-alkyl, *tert.*-alkyl, triphenylmethyl, hydrogen, there will

* The authors feel that, in spite of the disadvantages of introducing yet another set of symbols, this nomenclature is required since it is more general than that used by Ingold and his co-workers (*Trans. Faraday Soc.*, 1941, **37**, 686) or Dewar ("Electronic Theory of Organic Chemistry," Oxford Univ. Press, p. 111) for the hydrolysis of carboxylic acid esters.

be a tendency for a change in mechanism in the sense $S_{NX}1 \longrightarrow S_{NX}2 \longrightarrow S_{NC}2 \longrightarrow S_{NC}1$ as we proceed from left to right. With any one given acid the range of groups in the above series is insufficient to show the whole sequence of changes, and the series has not been extended sufficiently to the left to show the mechanism $S_{NX}1$. For many acids, portions of the sequence have been observed, as will be discussed later.

TABLE 1.

Ester	Fission by scheme :	Ester	Fission by scheme :
tert.-Butyl hypochlorite	2	*n*-Butyl nitrate	mixed
tert.-Butyl hypobromite	2	*n*-Octyl nitrate	mixed
Triphenylmethyl hypochlorite	2	*tert.*-Butyl nitrate	1
„ chlorate	2	Triphenylmethyl nitrate	1
„ bromate	2	Bistriphenylmethyl sulphate	1
„ iodate	2	Diethyl sulphate	mixed
„ perchlorate	1	Di-*tert.*-butyl chromate	2
n-Butyl nitrite	2	Bistriphenylmethyl chromate	mixed
tert.-Butyl nitrite	2	*tert.*-Butyl acetate	2
Triphenylmethyl nitrite	2	Triphenylmethyl acetate	mixed

It is clear from the above considerations that if the triphenylmethyl ester of a given acid is hydrolysed by an S_{NX} mechanism (scheme 2) the hydrolysis of all esters of the same acid to the left of triphenylmethyl in the series above will also follow the same mechanism. Table 1 shows that the triphenylmethyl esters of hypohalogenous, halogenic, and nitrous acids are hydrolysed by mechanism S_{NX}, probably by a bimolecular nucleophilic attack on atom X. It may therefore be safely concluded that all other esters of these acids will also hydrolyse by the same mechanism, typified by $RO \dotplus ClO^1$.

Influence of Acid Strength.—Examination of Table 1 shows that, in general, esters hydrolysing by mechanism 2 are those of weak inorganic acids. With esters of strong acids, a rough correlation may be expected between the strength of the acid, which is a measure of its tendency to given up a proton, and the ease of alkyl–oxygen fission. In fact, the esters of the strongest acids and very electropositive alkyl groups are known to be partially ionic (Hantzsch, *Ber.*, 1930, **63**, 1181; 1921, **54**, 2573).

For this reason triphenylmethyl perchlorate, sulphate, and nitrate are hydrolysed with alkyl–oxygen fission, presumably by an $S_{NC}1$ mechanism.

However, Bodforss and Ahrland (*loc. cit.*) report that the hydrolysis of triphenylmethyl perchlorate is subject to both acid and alkaline catalysis. This is inconsistent with our isotopic results unless one assumes a nucleophilic attack on the α-carbon atom of the triphenylmethyl group, which is most unlikely. Our attempts to repeat their work and measure the rate of hydrolysis of this perchlorate were unsuccessful owing to the almost instantaneous reaction.

In a series of esters of an inorganic acid where the alkyl group is progressively replaced by less electropositive groups, a change in mechanism from 1 to 2 will occur at some point. This point will be reached earlier for the weaker acids and it may require a very electronegative group to cause a change in mechanism in the hydrolysis of esters of the stronger acids.* Thus in the case of the chromates and acetates a change in mechanism already occurs in passing from triphenylmethyl to *tert.*-butyl. This conclusion is borne out by the work of Kenyon and his co-workers, who used optically active carboxylic esters of certain secondary alcohols (Kenyon and Mason, *J.*, 1952, 4964 and previous papers). They observed that small changes in conditions are sufficient to change the mode of bond fission.

In the hydrolysis of esters of a stronger acid, such as nitric acid, the isotopic results show that the change in mechanism occurs with the normal alkyl ester.

Baker and Easty (*loc. cit.*) have observed bimolecular alkaline hydrolysis of normal alkyl nitrates and have assumed a nucleophilic attack on carbon. Their results should be reinterpreted in terms of the present work as involving nucleophilic attack also on nitrogen. This interpretation is supported by the work of Ansell and Honeyman (*J.*, 1952,

* In acid media a similar situation prevails except that the change in mechanism occurs earlier. Hydrolysis in acid media will form the subject of a separate paper.

2778) on the hydrolysis of sugar nitrates and of Horne and Shriner (*J. Amer. Chem. Soc.,* 1933, **55**, 4652) on the nitration of cyclic ketones with optically active nitrates.

Bunton and Frei's results (*J.,* 1951, 1872) show that the alkaline hydrolysis of phenyl toluene-*p*-sulphonate occurs by scheme 2. On the other hand, we have found that *n*-alkyl sulphates are hydrolysed mainly with alkyl–oxygen fission. In view of the close similarity in the strength of toluene-*p*-sulphonic acid and sulphuric acid it may be concluded that in the sulphates a change in mechanism probably occurs between the phenyl and the *n*-alkyl groups.

On comparing the triphenylmethyl esters of oxyacids of a given element varying in the degree of oxidation of the oxyacids, a tendency for the ester of the highest oxidation state, *i.e.*, corresponding to the strongest acid, to hydrolyse by mechanism 1 is evident, whereas those of the lower oxidation state react by scheme 2. For instance, in the series RO–Cl, RO–ClO (postulated), R–ClO_2, R–$OClO_3$, the change in mechanism occurs between chlorate and perchlorate. No chlorite esters are known but it can be safely assumed that all chlorites would be hydrolysed according to scheme 2.
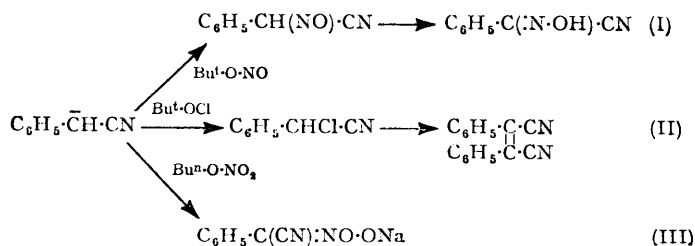
Similarly, in the oxyacids of nitrogen all nitrites react by mechanism 2 whereas tertiary nitrates react by mechanism 1, *i.e.*, $RO{\cdot}|{\cdot}NO$, $R{\cdot}|{\cdot}ONO_2$.

Cationic Reactions.—Other reactions of the esters of inorganic oxyacids may be related to the mechanism of alkaline hydrolysis, since, in the reaction schemes outlined above, the reagent Y may be any nucleophilic molecule and need not be limited to the hydroxyl ion. Thus reactions by scheme 1 (S_{NC}) will lead to ether formation if $Y = RO^-$ or to alkylation if $Y = {\geqslant}C^-$, or $>N^-$, while those proceeding by scheme 2 (S_{NX}) will lead to trans-esterification if $Y = RO^-$ and to halogenation, nitration, nitrosation, etc., if $Y = {\geqslant}C^-$ or $>N^-$. Numerous examples are available to illustrate these points. The use of dimethyl and diethyl sulphates as alkylating agents in alkaline media is well known, alkylation by *tert.*-butyl perchlorate has been reported (Cauquil, Barrera, and Barrera, *Bull. Soc. chim.,* 1953, **20**, 1111), and *N*-alkylation by triphenylmethyl nitrate and diphenylmethyl nitrate has recently been described by Cheeseman (*Chem. and Ind.,* 1954, 281).

The above esters have been shown to undergo hydrolysis by mechanism S_{NC}. Although it is the tertiary alkyl group which promotes reaction by this mechanism, the considerable steric hindrance associated with this group often limits the use of these esters as alkylating agents.

Halogenation by hypohalites has been discussed by Anbar and Ginsburg (*Chem. Reviews,* in the press). Nitration by *n*-alkyl nitrates and nitrosation by alkyl nitrites are well-known procedures (cf. Sidgwick, " Organic Chemistry of Nitrogen," Oxford Univ. Press, 1937, pp. 4, 8). These esters undergo hydrolysis by mechanism S_{NX}. As a further illustration, the action of *tert.*-butyl hypochlorite, nitrate, and nitrite and of *n*-butyl nitrate on benzyl cyanide in alkaline media has been examined.

From the reaction of the hypochlorite, diphenyl maleinitrile (II) was isolated. In the nitrite reaction the oxime (I) of phenylglyoxylonitrile was formed, and *n*-butyl nitrate gave a 70% yield of the sodium salt of *aci*nitrophenylacetonitrile (III). These results are consistent with the following reaction schemes :

$$C_6H_5{\cdot}CH(NO){\cdot}CN \longrightarrow C_6H_5{\cdot}C({:}N{\cdot}OH){\cdot}CN \quad (I)$$

$$\begin{array}{c} \nearrow Bu^t{\cdot}O{\cdot}NO \\ \nearrow Bu^t{\cdot}OCl \\ C_6H_5{\cdot}\bar{C}H{\cdot}CN \xrightarrow{\hspace{1cm}} C_6H_5{\cdot}CHCl{\cdot}CN \longrightarrow \begin{array}{c} C_6H_5{\cdot}C{\cdot}CN \\ \| \\ C_6H_5{\cdot}C{\cdot}CN \end{array} \quad (II) \\ \searrow Bu^n{\cdot}O{\cdot}NO_2 \\ \searrow \end{array}$$

$$C_6H_5{\cdot}C(CN){:}NO{\cdot}ONa \qquad (III)$$

tert.-Butyl nitrate, on the other hand, with benzyl cyanide in alcoholic sodium ethoxide gives a quantitative yield of sodium nitrate and some *tert.*-butyl ethyl ether. No nitration products could be isolated, indicating the absence both of any trans-esterification with the solvent and of direct nitration.

Trans-esterification and Oxidation Reactions.—Tertiary alkyl esters can undergo reactions only by schemes 1 and 2. In compounds hydrolysing by scheme 2 (Y = OR⁻) (see p. 3604), trans-esterification is always possible : RO⁻ + X–O–C ---→ ROX + ⁻O–C, and therefore in a mixture of a tertiary ester and a secondary or primary alcohol, a certain proportion of the ester of this alcohol will be formed. Once such an ester is formed, it will react further by schemes 2 and 3. Two possibilities exist for reaction by the latter scheme, namely, free-radical or ionic reactions. Under appropriate conditions, in the vapour or liquid phase and in solution in non-ionising solvents, the ester may decompose by a free-radical mechanism to give oxidation products (Waters, see Gilman, " Organic Chemistry," Vol. IV, Chap. 12, 1953; Kharasch, Fono, Nudenberg, and Bischof, *J. Org. Chem.*, 1952, **17**, 209 and previous papers; Steacie, " Atomic and Free Radical Reactions," Reinhold, 1946).

In alkaline aqueous media, for esters which are hydrolysed with alkyl–oxygen fission, olefin elimination by mechanisms $E1$ and $E2$ will compete with the substitution reaction in proportions which depend on the nature of the alkyl group and the conditions of reaction (Ingold, *op. cit.*, Ch. 8). On the other hand, for esters undergoing hydrolysis by mechanism S_{NX}, the reaction analogous to olefin formation is scheme 3 (cf. p. 3604), leading to oxidation products (see also Kornblum and De la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880) : Y⁻ + H·C·O·X ——→ YH + C=O + X⁻. This will occur only when the negatively charged group X⁻ is stable. Thus, whereas primary and secondary hypochlorites are oxidised, the corresponding nitrites are stable towards this reaction.

It follows that for a tertiary ester to be a useful oxidising agent for alcohols it should (*a*) undergo hydrolysis by scheme 2 and therefore be capable of trans-esterification, and (*b*) give a stable X⁻ group. Hence, tertiary perchlorates, sulphates, and nitrates, which are hydrolysed by scheme 1, are not oxidising agents since they do not fulfil condition (*a*). It should be noted that primary and secondary nitrates, which tend to hydrolyse by scheme 2, when formed by other methods give a certain proportion of oxidation products (Baker and Easty, *loc. cit.*; Lucas and Hammett, *loc. cit.*).

On the other hand, *tert.*-butyl nitrite and acetate, although undergoing trans-esterification, do not oxidise other alcohols since the groups NO⁻ and CH₃·CO⁻ are unstable. All other tertiary esters listed in Table 1 are oxidising agents in that they fulfil both the conditions outlined above; cf. *tert.*-butyl hypochlorite (Anbar and Ginsburg, *loc. cit.*; Grob and Schmid, *Helv. Chim. Acta*, 1953, **36**, 1763), chromate (Leo and Westheimer, *loc. cit.*), also the oxidation of *iso*propyl alcohol by bromate to acetone (Farkas and Uri, *Chem. Abs.*, 1951, **45**, 1498).

In addition to these reactions, rearrangements may accompany reactions proceeding by scheme 2. The rearrangement is analogous to that of Wagner and Meerwein, and involves an internal nucleophilic attack on oxygen :
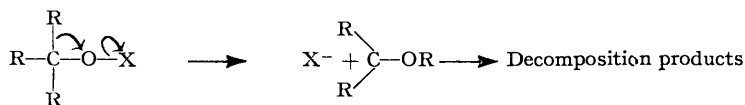
A similar mechanism has been suggested in the decomposition of certain hydroperoxides (Kharasch *et al.*, *loc. cit.*; Bartlett and Cotman, *J. Amer. Chem. Soc.*, 1950, **72**, 3095), and should be particularly prominent in triphenylmethyl esters analogously to the hydrolysis of triphenylethyl chloride (Charlton, Dostrovsky, and Hughes, *Nature*, 1951, **167**, 986). Triphenylmethyl esters which are hydrolysed by mechanism 1 do not of course undergo this rearrangement, and hydrolysis is clean. Similarly, the nitrite ester, provided no thermal decomposition sets in, is hydrolysed cleanly and gives a quantitative yield of the carbinol. On the other hand the hypochlorite, chlorate, bromate, and iodate give varying amounts of breakdown products such as benzophenone, diphenyl, and phenol.

EXPERIMENTAL

Preparation of Esters.—*tert.*-Butyl hypochlorite and hypobromite were prepared by the methods described by Anbar and Dostrovsky (*loc. cit.*).

Triphenylmethyl hypochlorite was prepared by shaking a suspension of triphenylmethanol

(1·3 g.) in a carbon tetrachloride solution of chlorine monoxide (30 ml.; 0·2M) in the presence of anhydrous sodium sulphate (10 g.). After 24 hours' shaking at room temperature, the solution was decanted and concentrated to half its volume in a vacuum. Some unchanged carbinol was filtered off, and the filtrate evaporated to dryness in a vacuum in a vessel protected from light. Golden-yellow crystals were obtained which were hydrolysed rapidly on exposure to moist air and were very soluble in carbon tetrachloride The substance is hydrolysed immediately in aqueous media and the solution is free from chloride ion but contains active chlorine as hypochlorous acid. From the hydrolysis mixture there were isolated in addition to the carbinol small quantities of benzophenone, diphenyl, and phenol.

Triphenylmethyl chlorate was prepared by shaking a solution of triphenylmethyl chloride (5 g.) in carbon tetrachloride (60 ml.) with silver chlorate (9 g.) for 12 hr. at room temperature. The silver chlorate was prepared from sodium chlorate and silver nitrate (" Inorganic Syntheses," Vol. II, p. 4). The yellow-orange solution was decanted and concentrated to dryness in a vacuum. Orange crystals were obtained which were free from chloride ion. The solution becomes brown-black on hydrolysis in alkali. The dark solution contained, in addition to the carbinol, oxidation and decomposition products.

Triphenylmethyl bromate and iodate were prepared by a method similar to that described above, by use of silver bromate and silver iodate, respectively. Both form orange crystals. In the case of triphenylmethyl iodate, ether was used as the solvent since this iodate is insoluble in carbon tetrachloride.

Triphenylmethyl perchlorate, prepared from 70% perchloric acid and triphenylmethanol in acetic anhydride (Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4861), was isolated as brown crystals.

Diethyl sulphate, *n*-butyl nitrite, and *tert.*-butyl acetate were commercial products and were purified by fractional distillation before use.

tert.-Butyl nitrite was prepared by a modification of the method in " Organic Syntheses " (Coll. Vol. II, p. 108), in which concentrated sulphuric acid was added slowly to a cooled aqueous solution of sodium nitrite and *tert.*-butanol.

Triphenylmethyl nitrite was prepared by the action of liquid dinitrogen trioxide at −10° on an ether solution of triphenylmethanol. The solution was concentrated to one third of its volume under vacuum, and the triphenylmethyl nitrite filtered off, washed with dry light petroleum, and dried in a vacuum (P_2O_5). This is a modification of the method used by Schlenk, Mair, and Bornhardt (*Ber.*, 1911, **44**, 1169). Analyses for the nitrite content of this ester by Griess's method gave values ranging between 80 and 90% for the conversion of carbinol into nitrite ester.

n-Butyl nitrate was prepared by reaction of *n*-butanol with nitric and sulphuric acids (Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 768). *n*-Octyl nitrate was prepared from octyl bromide and silver nitrate in acetonitrile (Ferris, McLean, Marks, and Emmons, *ibid.*, 1953, **75**, 4078). *tert.*-Butyl nitrate was prepared from *tert.*-butyl chloride and silver nitrate (Baker and Easty, *J.*, 1952, 1202). Triphenylmethyl nitrate was prepared by shaking an ether or carbon tetrachloride solution of triphenylmethyl chloride with silver nitrate until chloride ion was no longer detected. The carbon tetrachloride solution was yellow, and the ether solution colourless.

Di-*tert.*-butyl chromate was prepared in carbon tetrachloride from chromic oxide and *tert.*-butanol (Westheimer, *loc. cit.*). Bistriphenyl chromate was prepared by shaking a carbon tetrachloride solution of triphenylmethyl chloride with silver chromate. The red-orange solution is unstable and slowly decomposes.

Triphenylmethyl acetate, prepared from triphenylmethyl chloride and silver acetate (Gomberg, *Ber.*, 1902, **35**, 1835), had m. p. 86—88°.

Bistriphenylmethyl sulphate was prepared by shaking a carbon tetrachloride solution of triphenylmethyl chloride with silver sulphate.

In attempts to prepare *tert.*-butyl and triphenylmethyl permanganate by refluxing a carbon tetrachloride solution of the corresponding chloride with silver permanganate, no reaction was observed, even after 12 hr.

Attempts to prepare *tert.*-butyl iodate included shaking *tert.*-butyl chloride and silver iodate in carbon tetrachloride or acetonitrile solutions, refluxing *tert.*-butyl alcohol and iodine pentoxide in carbon tetrachloride, and shaking an aqueous solution of *tert.*-butanol and iodic acid in the presence of carbon tetrachloride. In no case did reaction occur.

[18]O-*Alkoxy-labelled Esters.*—[18]O-Labelled *tert.*-butyl nitrite, chromate, and hypochlorite were prepared by shaking ^{18}O-labelled *tert.*-butanol (cf. Anbar and Dostrovsky, *loc. cit.*) with an aqueous solution of the acid in the presence of dilute sulphuric acid and carbon tetrachloride.

After 4 hours' shaking at room temperature, the carbon tetrachloride layer was separated and washed with water until free from alcohol. The esters were not isolated and the solutions in carbon tetrachloride were used directly in further experiments. In each case a slow acid-catalysed exchange occurs between water and *tert.*-butanol (see Dostrovsky and Klein, *J.*, to be published). Therefore the unchanged alcohol from the aqueous layer was isolated and analysed for ^{18}O content as a check. In no case did the exchange amount to more than 5%.

^{18}O-Labelled nitrites were also prepared from ^{18}O-labelled *tert.*-butanol and liquid dinitrogen tetroxide at 0° (cf. Yoffe and Gray, *J.*, 1951, 1412), and from *tert.*-butanol and liquid nitrosyl chloride in pyridine at 0°. ^{18}O-Labelled *tert.*-butyl acetate was prepared from ^{18}O-labelled *tert.*-butanol, acetyl chloride, and pyridine in xylene solution by the method used by Bogart and Smith (*J. Amer. Chem. Soc.*, 1936, **58**, 1016) for the unlabelled ester.

Hydrolyses of Esters in ^{18}O-Labelled Water.—A 5N-sodium hydroxide stock solution was prepared from the required amount of a 3% sodium amalgam and water enriched in ^{18}O. This was diluted with enriched water as required.

The results of the isotopic experiments are summarised in Tables 2 and 3.

TABLE 2. *Hydrolysis of unlabelled esters in aqueous alkali labelled with* ^{18}O.

Ester	Atom % excess of ^{18}O in : hydrolysis medium	alcohol from hydrolysis	% Alkyl–oxygen fission	Ester	Atom % excess of ^{18}O in : hydrolysis medium	alcohol from hydrolysis	% Alkyl–oxygen fission
Bu^t·OCl	0·87	0·00	0	C$_8$H$_{17}{}^n$·O·NO$_2$	2·00	0·51	15
Bu^t·OBr	1·35	0·00	0	Bu^t·O·NO$_2$	1·35	1·35	100
Ph$_3$C·OCl	1·35	0·00	0	Ph$_3$C·O·NO$_2$	1·67 *	1·51	91
Ph$_3$C·O·ClO$_2$	1·35	0·01	1	(Bu^{t}O)$_2$CrO$_2$	1·35	0·05	4
Ph$_3$C·O·BrO$_2$	1·35	0·00	0	(Ph$_3$C·O)$_2$CrO$_2$	1·67 *	1·10	66
Ph$_3$C·O·IO$_2$ ...	1·35	0·01	1	Bu^t·OAc	2·00	0·08	4
Ph$_3$C·O·ClO$_3$	1·84	1·75	95	Ph$_3$C·OAc ...	1·32 *	0·88	67
Bu^n·O·NO ...	2·00	0·00	0	(Ph$_3$C·O)$_2$SO$_2$	1·67 *	1·56	93
Bu^t·O·NO ...	1·35	0·00	0	(EtO)$_2$SO$_2$ ...	1·72	1·47	85
Ph$_3$C·O·NO$_2$ ...	1·35	0·01	1	Ph$_3$C·OH † ...	1·35	0·00	0
Bu^n·O·NO$_2$ ...	1·35	0·44	33				

* Atom % excess ^{18}O in triphenylmethanol obtained by hydrolysis of stock triphenylmethyl chloride solution in the ^{18}O labelled medium.

† Control experiment showing absence of oxygen-exchange between triphenylmethanol and aqueous alkali.

TABLE 3. *Hydrolysis of ^{18}O-alkoxy-labelled esters in* N-*aqueous alkali.*

Ester	Atom % excess of ^{18}O in : alkoxy-group	alcohol from hydrolysis	% Alkyl–oxygen fission	Ester	Atom % excess of ^{18}O in : alkoxy-group	alcohol from hydrolysis	% Alkyl–oxygen fission
Bu^t·OCl	0·86	0·85	1	Bu^t·OAc	1·60	1·54	4
Bu^t·O·NO ...	1·60	1·59	0	(Bu^{t}O)$_2$CrO$_2$	1·60	1·42	10

(i) *n*-Butyl nitrite (2 g.) of normal isotopic composition was shaken for 14 days at room temperature with 2·5N-aqueous sodium hydroxide solution (20 ml.) enriched with respect to ^{18}O, and the aqueous layer separated and fractionated. The azeotrope of alcohol and water was dried (K$_2$CO$_3$). A second drying was carried out with vigorous shaking at 60° for 3 hr. The alcohol was then analysed for its ^{18}O content by Anbar, Dostrovsky, Klein, and Samuel's procedure (*J.*, in the press).

(ii) *n*-Butyl nitrate (3 g.) was dissolved in a mixture of N-aqueous sodium hydroxide (30 ml.) enriched in ^{18}O and absolute ethanol (40 ml.). The solution was refluxed for 8 days in a stainless-steel vessel and then extracted with carbon tetrachloride to remove unchanged nitrate ester. The aqueous layer was fractionated carefully, and the butanol dried and analysed as above. A similar procedure was used for *n*-octyl nitrate.

(iii) *tert.*-Butyl nitrate (1·2 g.) was shaken for 24 hr. with N-aqueous sodium hydroxide (10 ml.) enriched in ^{18}O. The alcohol was distilled out, dried, and analysed as above.

(iv) Diethyl sulphate * and *tert.*-butyl acetate were refluxed with N-aqueous sodium hydroxide enriched in ^{18}O. The aqueous layer was fractionated, and the alcohol dried and analysed.

(v) *tert.*-Butyl hypobromite was hydrolysed with aqueous sodium hydroxide enriched in ^{18}O according to the procedure for the hypochlorite (cf. Anbar and Dostrovsky, *loc. cit.*).

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(vi) *tert.*-Butyl chromate in carbon tetrachloride solution (10 ml., 0·5 ml.) was refluxed with 5N-aqueous sodium hydroxide (20 ml.) enriched in ^{18}O. The aqueous layer was extracted with carbon tetrachloride and fractionated. The alcohol was dried and anlysed as above. In the aqueous layer a quantitative amount of chromate was found by analysis as barium chromate.

(vii) *Hydrolysis of triphenylmethyl esters.* In the hydrolysis of triphenylmethyl esters the following procedure was used for the sulphate, nitrate, chromate, chlorate, bromate, and iodate. A stock solution of triphenylmethyl chloride (0·3M) in carbon tetrachloride was prepared. Aliquot portions (30 ml.) were shaken with the corresponding silver salt until reaction was complete, as judged by the absence of chloride ion upon the hydrolysis of a test sample. The carbon tetrachloride solution of the ester was decanted into an excess of 4N-aqueous solution of sodium hydroxide enriched in ^{18}O and shaken at room temperature until hydrolysis was completed. The carbinol formed, being only slightly soluble in the carbon tetrachloride, collected at the interface and was filtered off, washed with water and carbon tetrachloride, recrystallised from benzene, and analysed for ^{18}O by the method described below.

The aqueous phase resulting from the hydrolysis of the chromate ester was analysed for chromate gravimetrically as barium chromate. The amount obtained was in satisfactory agreement with the mass of carbinol isolated.

Triphenylmethyl acetate is hydrolysed very slowly unless the experiment is carried out as a homogeneous reaction. The ester was therefore prepared in dioxan as solvent from silver acetate and triphenylmethyl chloride and was refluxed for several days at 100°. In order to avoid errors due to the presence of small amounts of carbinol in the triphenylmethyl chloride solutions and to systematic errors in the analysis, portions of the triphenylmethyl chloride stock solution were hydrolysed with the same enriched sodium hydroxide solution and the ^{18}O content of the resulting carbinol was used in computing the percentage of alkyl–oxygen fission of the esters. Nevertheless, a small amount of decomposition occurs which leads to the formation of small quantities of carbinol and to slightly low results in the isotopic analysis. No oxygen exchange was detected in several experiments in which triphenylmethanol (2 g.) was refluxed with a mixture of ethanol (20 ml.) and aqueous sodium hydroxide enriched in ^{18}O (5 ml.; 1N). In the case of triphenylmethyl perchlorate, nitrite, and hypochlorite, the crystalline ester (3 g.) was shaken in excess of N-sodium hydroxide enriched in ^{18}O at room temperature until hydrolysis was complete, and the carbinol isolated and analysed.

The aqueous solution resulting from the hydrolysis of the nitrite ester was analysed for nitrite by Griess's method.

Analysis of Triphenylmethanol for ^{18}O content.—The ^{18}O content of the triphenylmethanol obtained from the hydrolysis experiments was determined as follows : Dry hydrogen chloride was bubbled through a benzene solution of the carbinol (1·5 g. in 12 ml. of dry benzene) for several minutes until all the carbinol was converted into triphenylmethyl chloride. The turbid solution was then centrifuged until the water (*ca.* 0·1 ml.) separated at the bottom. By means of a micro-pipette, 30 mg. of the water were introduced into a sealed tube, and the ^{18}O content of the water determined by equilibration overnight with carbon dioxide at 70°, and analysis of the carbon dioxide in a mass-spectrometer.

Hydrolysis of ^{18}O-Labelled Esters.—(a) The carbon tetrachloride solution of ^{18}O-labelled *tert.*-butyl nitrite and hypochlorite was shaken at room temperature with a large excess of N-sodium hydroxide for 14 days. The aqueous layer was then separated, extracted with carbon tetrachloride to remove unchanged ester, and fractionated. The azeotrope was treated with potassium carbonate, and the alcohol dried and analysed as before.

(b) A carbon tetrachloride solution (10 ml.; 0·5M) of ^{18}O-labelled di-*tert.*-butyl chromate was refluxed with excess of 5N-sodium hydroxide (20 ml.) for 12 hr. The carbon tetrachloride layer was washed several times with dilute sodium hydroxide and the combined aqueous phase was distilled. The azeotrope was treated as above.

(c) ^{18}O-Labelled *tert.*-butyl acetate was refluxed with 4N-sodium hydroxide for 5 days. After separation of the unchanged ester the aqueous layer was extracted with carbon tetrachloride, and fractionated. The azeotrope was treated as above and analysed.

Cationic Reactions.—*Nitrosation.* A mixture of benzyl cyanide (1·5 g.) and *tert.*-butyl nitrite (1·4 g.) was added slowly to a stirred solution of metallic potassium (0·8 g.) in *tert.*-butanol (20 c.c.). After a further 10 minutes' stirring, the solution was poured into a large volume of cold water, acidified, and extracted with ether. On evaporation of the ether, a solid remained which, crystallised from hot water (twice; 1 g.; m. p. 128°), was identified as the oxime of phenylglyoxylonitrile (cf. Wislicenus, *Ber.*, 1888, **21**, 1314).

Nitration. A mixture of benzyl cyanide (1·2 g.) and *n*-butyl nitrate (1·2 g.) was added with

stirring to an ice-cold solution of sodium (0·25 g.) in dry ethanol (10 g.). A white precipitate (0·8 g.) was formed which was identified as the sodium salt of *aci*-nitrophenylacetonitrile (cf. *idem, Ber.*, 1902, **35**, 1755).

When a mixture of *tert.*-butyl nitrate (2·3 g.) and benzyl cyanide (2·3 g.) was added slowly to an ice-cold solution of sodium (0·5 g.) in dry ethanol (20 c.c.), an immediate precipitate (1·5 g.) was formed which was identified as sodium nitrate. The filtrate was poured into water (100 ml.) saturated with sodium sulphate and extracted with ether. The ether layer was dried and fractionally distilled. A small quantity of *tert.*-butyl ethyl ether, b. p. 66—67°, was obtained.

From a parallel experiment unchanged benzyl cyanide (1 g.) was recovered from the ethanolic solution upon fractionation. No ethyl nitrate could be detected in the products of the alcoholysis of *tert.*-butyl nitrate.

Chlorination. An ice-cold mixture of benzyl cyanide (2 g.) and *tert.*-butyl hypochlorite (2·5 g.) was slowly added with stirring to an ice-cold solution of potassium (0·8 g.) in *tert.*-butanol (10 ml.). The solution became dark brown and stirring was continued for 1 hr. The precipitate was filtered off and distilled *in vacuo*. At 200—210°/5 mm. a light yellow liquid distilled over, which solidified. The solid was recrystallised from benzene and identified as diphenyl-maleinitrile (0·5 g.; m. p. 150°) (cf. Michael and Jeanpretre, *Ber.*, 1892, **25**, 1681).

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