eq A-42 is given by

$$\text{slope/intercept} = \frac{k_{-1}}{k_2}\frac{K_{\text{ROH}}}{(a_{\text{H}})^2} \qquad \text{(A-43)}$$

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Dialkoxycarbonium Ions as Ambident Electrophiles in Their Hydrolysis in Aqueous Sulfuric Acid Solutions

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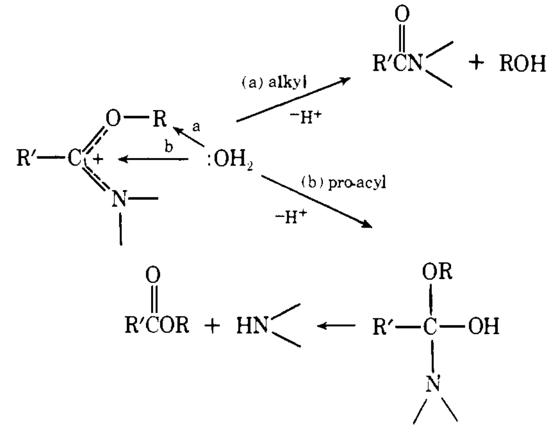
Abstract: The dimethoxy-2,4,6-trimethylphenylcarbonium ion (II) hydrolyzes with cleavage of both the methyl carbon-oxygen bond and the pro-acyl carbon-oxygen bond, the amount of former increasing with increasing sulfuric acid concentration. The dimethoxyphenylcarbonium ion (I) cleaves only the pro-acyl carbon-oxygen bond at all acidities. These results are compared with those obtained for analogous imidatonium ions, where alkyl carbon-oxygen bond cleavage is more dominant. It is concluded that dealkylation of alkoxycarbonium ions is more important for a less reactive (or more stable) cation. The possibility of observing $A_{Al}2$ carboxylate ester hydrolysis is considered.

Recently we have demonstrated[1,2] that there are two routes for the acid-catalyzed hydrolysis of imidate esters, differentiated by the position of nucleophilic attack of a water molecule on the imidatonium ion (Scheme I).

Scheme I



In this paper will be reported an evaluation of the importance of the dealkylation reaction in the hydrolysis of methylated and protonated carboxylate esters, in other words, an evaluation of the importance of $A_{Al}2$ carboxylate ester hydrolysis as compared to the normal $A_{Ac}2$ mechanism.[3] According to the imidate results,[2] the type of ester for which the former reaction is most likely to occur, if at all, is the methyl ester of a sterically congested carboxylic acid, for example, a 2,6-dimethylbenzoate. Such esters, however, appear not to undergo bimolecular hydrolyses in acid solutions, preferring a unimolecular route via the acylium ion.[4]

We have turned therefore to what might be considered as models for carbonyl protonated esters, dialkoxycarbonium ions $R'C^+(OR)_2$.[5] These can be conveniently prepared from the ortho ester ($R'C(OR)_3$) either as a salt with a weakly nucleophilic counterion,[6] or on solution in strong acid media.[7] A number of studies[5,7,8] of the NMR spectra of these species, along with various other properties, have now appeared, and their hydrolysis does give the expected products of ester and alcohol.[6] For our purposes these are ideally suited since there is little possibility for unimolecular reactions providing that the alkoxy group consists of a primary alkyl group. The ap-

Table I. Rates of Hydrolysis of Dimethoxycarbonium Ions I and II in Aqueous H_2SO_4 Solutions at 25 °C

I		II			
% H_2SO_4	k_{obsd}, s^{-1}	% H_2SO_4	k_{obsd}, s^{-1}	k_{Ac}[a]	k_{Al}[a]
72.6	0.225	10.7	0.66	0.56	0.10
74.5	0.0992	20.8	0.43	0.35	0.08
76.4	0.0330	26.3	0.266	0.213	0.053
79.0	0.00940	31.4	0.155	0.123	0.032
80.9	0.00346	35.3	0.0885	0.0681	0.0204
83.4	0.00101	40.9	0.0389	0.0284	0.0105
85.2	0.000281	45.1	0.0189	0.0130	0.0059
88.2	0.000052	51.0	0.00565	0.00322	0.00243
		55.1	0.00263	0.00126	0.00137
		60.0	0.001015	0.000345	0.00670
		62.6	0.000590	0.000160	0.000430
		66.2	0.000204		
		69.9	0.000085		
		72.6	0.000045		

[a] Components of k_{obsd} corresponding to acyl carbon-oxygen and alkyl carbon-oxygen bond cleavage.

Scheme II

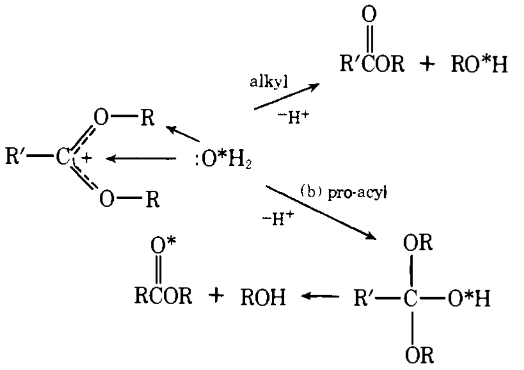


Table II. Activation Parameters for Hydrolysis of Ions I and II in Aqueous H_2SO_4 Solutions

Ion	% H_2SO_4	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
II	31.4	12.4	−20.7
II	40.9	13.4	−20.0
II	51.0	16.6	−12.9
II	60.0	17.8	−11.6
II	66.2	19.3	−10.6
I	76.5	13.6	−19.7
I	80.9	15.9	−18.1
I	85.6	19.4	−19.4

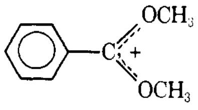
Table III. Tracer Study of Position of Bond Cleavage during Hydrolysis of Dimethoxy-2,4,6-trimethylphenylcarbonium Ion (II) at 25 °C

% H_2SO_4	Solvent % ^{18}O[a] (A)	Product % ^{18}O[b] (B)	Alkyl-oxygen cleavage, %[c]
0	3.32	2.73	14
19.4	2.79	2.33	18
40.0	2.16	1.65	26
44.0	2.03	1.48	30
48.7	1.87	1.24	38
56.1	1.62	0.83	57
60.0	1.47	0.63	66
63.8	1.34	0.48	75

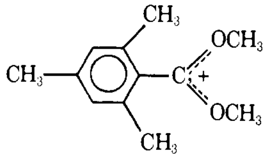
[a] See Experimental Section. [b] Error ±0.05. [c] 100 $(A - B)/(A - 0.2)$.

propriate labeling experiment should then permit a direct comparison of the two bimolecular routes (e.g., Scheme II).

In particular, we compare here the hydrolysis of two ions, the dimethoxyphenylcarbonium ion (I) and the dimethoxy-



I



II

2,4,6-trimethylphenylcarbonium ion (II), the sterically hindered II being an obvious candidate for an $A_{Al}2$ type of reaction.[9]

Results

The ions I and II hydrolyze cleanly in water and aqueous sulfuric acid solutions producing methanol and the appropriate methyl ester. First-order rate constants for the hydrolyses are listed in Table I as a function of acid concentration, and activation parameters obtained at selected acidities are given in Table II. These hydrolyses proved to be very rapid, with the rates showing a strong inverse dependency on acid concentration. The minimum acidity at which rates could be obtained for I was 72% H_2SO_4, for II 10% H_2SO_4. A more detailed investigation of dialkoxycarbonium ion reactivity is currently underway, and the results will be presented elsewhere.

The nature of the bond cleavage in the hydrolysis of II is summarized in Table III. This study was carried out as indicated in Scheme II, by allowing unlabeled dialkoxycarbonium ion to hydrolyze in labeled media, precautions being taken to ensure complete equilibration of oxygen-18 between water and sulfuric acid molecules[10] beforehand. The methyl mesitoate product was isolated and analyzed for oxygen-18 directly using the relative intensities of the parent + 2:parent ion peaks in the mass spectrometer. A substantial amount of alkyl-oxygen bond cleavage is observed for this hindered ion, the actual figure depending quite strongly on acid concentration.

In Table I the observed rate constant for hydrolysis of II is broken up into component parts corresponding to the two different cleavages. Although their relative sensitivity to changing acid concentration is different, the two reactions still show the overall trend of a decreasing rate with increasing acidity. It can also be commented here that the process occurring by alkyl carbon-oxygen cleavage appears to be accompanied by a less negative entropy of activation, as indicated

Table IV. Tracer Study of Position of Bond Cleavage during Hydrolysis of Dimethoxyphenylcarbonium Ion (I) at 25 °C

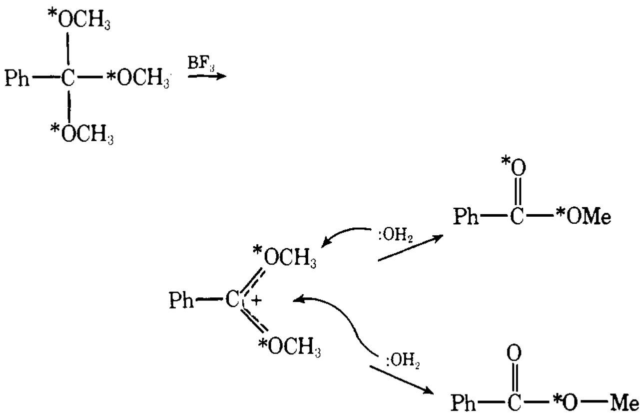
	Methyl benzoate rel intensities		Methyl benzoate excess % ^{18}O	
% H_2SO_4	107/105	138/136	C=O[a]	OCH_3[b]
0	0.0058	0.0537	0.00	4.33
69.0	0.0059	0.0538	0.00	4.33
80.0	0.0059	0.0527	0.00	4.23
Unlabeled sample	0.0057 (0.0045)[c]	0.0083 (0.0075)[c]		

[a] Based on 107:105 ratios. [b] Based on 138:136 ratios and conclusion of no excess ^{18}O in C=O. [c] Values based on natural abundance isotopic variation.[27]

by the change in $\Delta S^\ddagger$ for II as the acidity is increased (Table II) and this reaction becomes more favored.

For ion I the alternate approach of hydrolyzing a labeled ion in unlabeled solvent was employed. For this purpose a sample of labeled trimethyl orthobenzoate was prepared by mixing the ortho ester with methanol-^{18}O in the presence of a trace of acid, mass spectrometric analysis giving an ^{18}O content of 4.58% per oxygen in the ortho ester. The subsequent experimental procedure and the two possible labeling patterns in the methyl benzoate product are indicated in Scheme III.

Scheme III



Methyl benzoate proved to be analyzable in the mass spectrometer for both oxygens, the parent:parent + 2 peaks producing an overall picture, and the 105:107 peaks, which correspond to $[PhC{=}O]^+$, giving the carbonyl oxygen alone. The results are presented in Table IV and are only consistent with complete pro-acyl carbon-oxygen bond cleavage in the acids studied. Unfortunately the study could not be extended to more concentrated acids since the ester is no longer stable[11] and the ultimate product, benzoic acid, is expected to undergo rapid ^{18}O exchange.[12] It can be noted here that the $\Delta S^\ddagger$ values for I (Table II) are consistent with the observed cleavage, being of the same order as the values for II in dilute acid. The fact that these $\Delta S^\ddagger$ values are still as negative in the more concentrated acid also rules out a solvent effect[13] as the explanation for the variation with ion II.

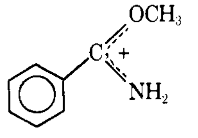
Because of the tendency for ester dealkylation to be favored by high temperatures and high acid concentrations (see later discussion and ref 2) we have checked the position of bond cleavage for methyl benzoate hydrolysis in 69% H_2SO_4 at 67 °C (conditions under which a bimolecular mechanism is known to be involved[11,14]). A sample of ester containing 11.98% ^{18}O in the ether oxygen was allowed to hydrolyze under these conditions for 2 half lives of hydrolysis (24 min). The methanol product, analyzed as its *p*-nitrobenzoate, was found to contain 12.04% ^{18}O, implying complete acyl carbon-oxygen bond cleavage.

Discussion

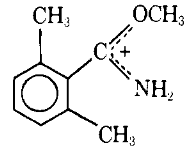
The basic finding of this work is that ion II undergoes, in part, hydrolysis by a mechanism which must be considered directly analogous to an $A_{Al}2$ acid-catalyzed ester hydrolysis, the only unobserved[3a] mechanism for this reaction. Evidence for the presence of this reaction, along with the normally observed bimolecular process occurring with acyl carbon-oxygen fission, is threefold: (a) the labeling experiments; (b) the negative entropies of activation of all acidities regardless of the predominant reaction; and (c) the inverse dependency on acidity of the rates for both reactions, (b) and (c) being indicative of bimolecular processes involving water.

In observing this reaction, there can be noted some common behavior shown by dialkoxycarbonium ions and imidatonium ions.[2] Dealkylation becomes more favored as the acidity is increased and also has a significantly less negative entropy of activation. These two general tendencies have a common origin, as explained previously,[2] in the differing solvation requirements of the transition states for the two reactions, the common behavior exhibited by the two different classes of compounds being indicative of similar transition states[15] in both systems.

There is, however, a major difference. In the imidatonium system the ion III showed a substantial amount of dealkylation, particularly at higher acidities,[1] and the sterically congested IV hydrolyzed to an extent >99% by this reaction at all acidities.[2] In the dialkoxycarbonium ion series, both the ion I and protonated methyl benzoate, two species which might be considered analogues of III, give *no* $A_{Al}2$ type of hydrolysis at any acidity, while the ion II, an analogue of IV, displays only a very finely balanced competition between the two routes. Thus, in general, in the dialkoxycarbonium ions, dealkylation appears to be a much less important reaction.



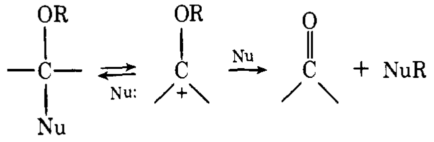
III



IV

The explanation behind this would appear to lie in relative reactivities, a collection of which is given in Table V. There is obviously a very great difference in reactivity in the two types of ions, the much diminished reactivity of the imidatonium ions being due to the stabilizing effect of the nitrogen atom adjacent to the cationic center. Additionally, however, the relative responses of the two bimolecular processes to this reactivity change are substantially different. In comparing III and I, substrates where acyl cleavage occurs, the reactivity difference is 10^9, but with IV and II, substrates where demethylation occurs, it is only 10^5. This would suggest that the more reactive the cation, the smaller is its tendency for dealkylation.

This same observation has been made by Hunig[16] in studies of reactions of various nucleophiles with similar ambident cations. He proposed that as the cation becomes more stable, and thus less reactive, the reaction involving attack at central carbon becomes reversible. This allows the system to channel out through the irreversible S_N2 process.



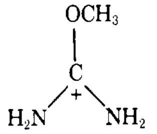
$$-\overset{\text{OR}}{\underset{\text{Nu}}{\overset{|}{\underset{|}{C}}}}- \underset{\text{Nu:}}{\rightleftarrows} \overset{\text{OR}}{\overset{|}{C^{+}}} \xrightarrow{\text{Nu}} \overset{\text{O}}{\overset{\|}{C}} + \text{NuR}$$

In a hydrolysis reaction, however, the tetrahedral species is not stable but can break up in other ways. If the Hunig argument were to apply here, its formation would have to be completely reversible. This is not the case. Substantial evidence has accumulated for imidate ester hydrolysis[17] that the formation of the intermediate is rate determining and irreversible. For the dialkoxycarbonium ions, the question of reversibility hinges around the leaving tendencies of OH vs. OR, and these should be similar, with perhaps a slight preference to OR.[18] A small amount of reversibility may be occurring then, but it cannot be, we feel, of any importance in explaining the differences found in this study.

In other words, we propose that the relative reactivities listed in Table V are a direct reflection of rates of water attack, and the trend displayed by the competing bimolecular reactions is a direct reflection of the electrophilicity of the two carbon atoms to the water molecule. Thus we conclude that the less stable an alkoxycarbonium ion is, the greater is its tendency for water attack at the central or pro-acyl carbon.

In simple terms this would seem to be accountable for by the extent of charge delocalization in the cation. The pro-acyl carbon is part of the π-bonding network, and the amount of positive charge actually localized at that position would be expected to show considerable variation. Thus large differences in the rate of water attack at that carbon are expected. The alkyl carbon, on the other hand, is not part of the π-bonding network, and thus shows a diminished sensitivity to stability or delocalization.

An additional case has been observed which seems to further verify this conclusion, in that the highly stabilized and very unreactive ion V hydrolyzes with dealkylation in dilute acids.[19]



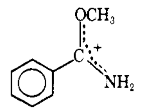
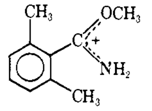
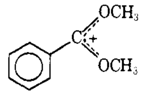
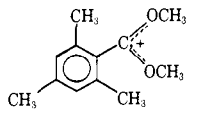
V

Interestingly this ion protonates in more concentrated acids, and the resultant dication, which now must be regarded as a more reactive species, is apparently attacked at the central carbon.

It should also be pointed out that the above conclusion is, in a sense, opposite to that made in a standard text,[20] where a comparison is made of the position of water attack in a series of esters with different central atoms (carboxylates, phosphates, sulfates, etc.). There could, of course, be a major difference since our comparison is based on the same central atom. We note, however, that acylic protonated phosphates and phosphinates, which must be considered as less reactive species than protonated carboxylates,[21] also show a greater tendency to dealkylation.[21,22]

Finally, a comment can be made regarding the relative importance of $A_{Al}2$ carboxylate ester hydrolysis. First of all, we note the comparatively[23] fast rate at which the demethylation of II occurs, and presumably also the dealkylation of a protonated carboxylate ester. For example, the S_N2 hydrolysis of II in water at 25 °C occurs at a rate 10^4-10^5 greater than the rate of hydrolysis of methyl tosylate.[23] In other words, neutral carboxylate esters and carboxylic acids must be considered as excellent leaving groups. On the other hand, this study shows that the rate of water attack at the acyl carbon of a protonated ester is so much more rapid that, despite this excellent leaving group, the dealkylation simply cannot compete. Possibly exceptions to this are esters with severe steric hindrance around the carbonyl carbon, but such molecules generally have another way out, the $A_{Ac}1$ reaction.[4] There is then a very close balance between competing reactions. Unhindered esters do not dealkylate because of the very rapid water attack at the central carbon; hindered esters do not dealkylate because of acylium ion formation. The conclusion then is that the $A_{Al}2$ reaction will not be observed, except perhaps for the case of a sterically congested ester which would give a destabilized acylium ion.

Table V. Rates of Hydrolysis of Imidatonium Ions and Dialkoxycarbonium ions in 50% H_2SO_4 at 25 °C

	Ion	Cleavage	Rate constant, s^{-1}
III		Mainly[a] pro-acyl	$3 \times 10^{-7 b}$
IV		Alkyl	$10^{-8 c}$
I		Pro-acyl	$2 \times 10^{2 d}$
II		Pro-acyl Alkyl	4×10^{-3} 3×10^{-3}

[a] See ref 1 and 2. [b] C. R. Smith and K. Yates, *J. Am. Chem. Soc.*, **94**, 8811 (1972). [c] Reference 2, extrapolated from higher temperatures. [d] Extrapolated from higher acidities.

Experimental Section

Materials. Aqueous sulfuric acid solutions were prepared and standardized as previously described.[24] Aqueous sulfuric acid solutions containing excess ^{18}O were obtained by cautious mixing of ^{18}O water (3.32% ^{18}O, Miles Laboratories) and 96.0% H_2SO_4, final concentrations being calculated from relative weights. Since H_2O and H_2SO_4 are known to exchange oxygen,[10] isotopic equilibration was ensured by placing these solutions in sealed vials and heating at 120 °C for 60 h before use. The ^{18}O content of the water in these solutions (for example, Table III) was then taken as an averaged value over all oxygens present.

Methanol-^{18}O was prepared as previously described,[25] using 12.2% ^{18}O water (Miles Laboratories). Methyl benzoate-*ether*-^{18}O was prepared from methanol-^{18}O and benzoyl chloride.

Dimethoxyphenylcarbonium tetrafluoroborate was prepared from trimethyl orthobenzoate and boron fluoride ethyl ether,[6c] while solutions of I in 100% H_2SO_4 were obtained on addition of the ortho ester to that acid;[7] NMR (external Me_4Si) τ 1.5-2.0 (5 H, m, ArH), 4.83 (6 H, s, CH_3). (A peak integrating to 3 H is also present at τ 4.57; this corresponds to the signal given by MeOH in 100% H_2SO_4).

Dimethoxyphenylcarbonium tetrafluoroborate-^{18}O was prepared from trimethyl orthobenzoate-^{18}O and boron fluoride ethyl ether. The labeled ortho ester was prepared by mixing trimethyl orthobenzoate (5 g) and methanol-^{18}O (2 g), with a trace (0.05 g) of *p*-toluenesulfonic acid. After standing for 3 h, the solution was neutralized (Na_2CO_3) and distilled.

The tetrafluoroborate salt of dialkoxycarbonium ion II precipitates as a white solid on dropwise addition of boron fluoride etherate to an equimolar amount of trimethyl orthomesitoate in dry ether. This salt was characterized by its NMR spectrum in 100% H_2SO_4, as reported below.

A stable solution of II in 100% H_2SO_4 was obtained by adding the ortho ester to that acid: NMR (external Me_4Si) τ 2.47 (2 H, broad singlet, ArH), 4.97 (6 H, s, OCH_3), 7.18 (3 H, s, *p*-CH_3), 7.27 (6 H, s, *o*-CH_3). An additional peak is seen at τ 4.57, as in the unsubstituted species above; this peak is absent in the NMR spectrum taken directly on the BF_4^- salt.

Trimethyl orthomesitoate was prepared by treatment of 2,4,6-trimethylbenzotrichloride[26] with a slight excess of sodium methoxide in methanol. In our hands this procedure invariably resulted in a mixture of the ortho ester and methyl mesitoate, regardless of the reaction conditions. These were separated by spinning band distillation to yield a pure sample of trimethyl orthomesitoate.[9b]

Products. Hydrolysis of both I and II gave rise to the expected product of methyl carboxylate and methanol. The presence of the latter was verified by NMR spectroscopy directly on hydrolyzed solutions. The presence of the former was verified by comparison of UV spectra with those of authentic samples, and, in selected cases, by methylene chloride extraction and GC analysis. Exceptions to this behavior occur in more concentrated acids (>85% H_2SO_4 for I, >65% H_2SO_4 for II) where the ester hydrolysis rate[4c,11] exceeds that of the dialkoxycarbonium ion and carboxylic acid is the observed product.

Kinetics. Hydrolyses were followed by UV spectroscopy on a Unicam SP 1800 spectrophotometer, observing the decrease in the peak due to the dialkoxycarbonium ion at 265 nm for I and 280 nm for II. Runs were initiated in general by addition of approximately 0.01 mL of an 0.1 M solution of the dialkoxycarbonium ion in 100% H_2SO_4 directly to the preequilibrated UV cell containing the acid solution (ca 2.5 mL). In several cases the BF_4^- salt itself was employed directly, and showed no difference. Plots of ln $(A - A_\infty)$ vs. time were linear for several half-lives, and the rate constants were obtained from their slopes by the method of least squares. Duplicate runs were carried out in all cases, with a general reproducibility in the observed rate constants of greater than 2%. Solutions in which the ester product underwent further hydrolysis presented no problem since there is little spectral change due to this reaction at the wavelengths employed.

Isolation of Products in Tracer Studies on I and II. For I, the freshly prepared ^{18}O-labeled BF_4^- salt (0.2 g) was added to normal abundance aqueous H_2SO_4 (20 mL) and for II freshly prepared unlabeled salt (0.2 g) was added to labeled solvent (3–5 mL). After a time corresponding to about 10 half-lives of hydrolysis the mixtures (the ester remaining in solution only in the more concentrated acids) were extracted with methylene chloride, the extract was washed with Na_2CO_3 and dried briefly with $MgSO_4$, and the solvent was removed. The small amount of remaining liquid was found by NMR to be pure ester, and was subjected directly to mass spectrometric analysis with no further purification.

Methyl Benzoate Cleavage. The labeled ester (0.25 mL) was dissolved in 20 mL of 69.0% H_2SO_4 acid preequilibrated at 67 °C and the solution placed in an oil bath for the selected time period, at which point it was withdrawn and the reaction quenched in ice. The methanol product was then isolated as its *p*-nitrobenzoate, using a procedure which is described elsewhere.[27]

Mass Spectrometric Analysis. All samples were analyzed directly on an AEI Model MS 902 mass spectrometer[28] equipped with a Vacuumetrics ratiometer. In general, the intensity ratio of two peaks in the mass spectrum of each sample was determined as the average of 40–50 readings, the reproducibility within one set of readings being ±0.0002, the reproducibility between different readings on the same sample being ±0.0004.

Methyl mesitoate was analyzed as the intensity ratio of peaks at 180:178 (P + 2:P). The values of % ^{18}O quoted in Table III for this compound were computed from the equation

$$\%\,^{18}\mathrm{O} = 99.8\left(\frac{R - R_0}{1.002 + R - R_0}\right) + 0.2 \qquad (1)$$

where R refers to the ratio of peaks in the product in question, and R_0 refers to the ratio in an unlabeled sample. This formula applies to a molecule in which only one oxygen can be enriched with ^{18}O, and corrects the intensity ratio for contributions due to naturally occurring isotopes in other positions.[29] The values of R_0 were determined in conjunction with the measurements of R and agree within 0.001 with predicted values.[30]

Trimethyl orthobenzoate displays no parent ion in its mass spectrum, but strong peaks at 151 ($C_6H_5C^+(OMe)_2$) and 105 ($C_6H_5C^+{=}O$) are present. The ratio 107:105 in the labeled sample of this compound is 0.0511, unlabeled material 0.0049; application of eq 1 gives 4.58% ^{18}O or 4.38% excess ^{18}O. The 153:151 ratio, labeled 0.1076, unlabeled 0.0081, is consistent with this, taking into account that there are now two oxygens which are enriched.

Methyl benzoate was analyzed at 107:105 ($C_6H_5C^+{=}O$) and 138:136 (parent). The sample prepared by reaction of benzoyl chloride (unlabeled) and methanol-^{18}O shows no variation in the former intensity ratio with that of unlabeled ester, with the excess ^{18}O showing up only in the parent ion peaks, implying that there is no scrambling of the two oxygens in the mass spectrometer. In Table IV, the observation that the 107:105 ratios in the products of hydrolysis of labeled ion are identical with the ratio in an authentic unlabeled sample implies that there is no ^{18}O enrichment in the carbonyl oxygen, and it must be derived from solvent. The enrichment observed in the 138:136 ratio can be attributed solely to the ether oxygen, which arises from labeled ion, and the calculated ^{18}O contents (eq 1) are consistent.

Methyl *p*-nitrobenzoate was analyzed using the parent ion at 183:181; ^{18}O contents were calculated according to eq 1.

In conclusion, it should be noted that all the calculations are based on the assumption of negligible $^{18}O/^{16}O$ kinetic isotope effects, both in the chemical reactions and in the mass spectrometer.

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