An Isotope Effect Study of the Acetolyses of Some Triphenylcarbalkoxymethylphosphonium Salts[1,2]

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Abstract: ^{13}C and ^{18}O kinetic isotope effects in the carbon dioxide formed during acetolysis of three triphenylcarbalkoxymethylphosphonium salts have been determined. Accompanying formation of carbon dioxide from triphenylcarbobenzhydryloxymethylphosphonium bromide (I) are ^{13}C and ^{18}O isotope effects of 1.045 and 1.015, respectively. Triphenylcarbooctyloxymethylphosphonium bromides (II and III) under similar conditions, yield carbon dioxide attended by no observable isotopic oxygen fractionation and a smaller ^{13}C isotope effect (1.020) than that observed during acetolysis of I. Exact calculations with various transition-state models support solvent-assisted heterolysis of I into benzhydryl carbonium ion, carbon dioxide, and methylenetriphenylphosphorane. Similar considerations lend support to a mechanism whereby II or III in acetic acid–acetic anhydride undergoes rate-controlling acetyl anhydride formation followed by the production of carbon dioxide, triphenylmethylphosphonium bromide, and acetic anhydride.

The thermolysis of triphenylcarbalkoxymethylphosphonium salts proceeds at relatively mild temperatures to yield carbon dioxide, an olefin, and triphenylmethylphosphonium halides.[3] During the course of the investigation of these decompositions, it was noted that heating triphenyl(carbo-*n*-octyloxymethyl)phosphonium bromide (II) in the presence of ammonium bromide yielded *n*-octyl bromide, carbon dioxide, and triphenylmethylphosphonium bromide. When the salt

$$\underset{\text{II}}{(C_6H_5)_3P^+CH_2CO_2C_8H_{17}} + 2Br^- \longrightarrow$$
$$(C_6H_5)_3P^+CH_3 + Br^- + CO_2 + C_8H_{17}Br$$

was heated in *n*-octanol, the products were di-*n*-octyl ether, carbon dioxide, and triphenylmethylphosphonium bromide.[4] The products of these reactions suggested that the mechanism for their formation involves an SN2 attack on the α-carbon of the alkoxy group of the salt. These reactions were much faster than SN2 reactions on normal esters. It was suggested therefore that the transition states involve the formation of carbon dioxide and methylenetriphenylphosphorane.

More recent studies of the solvolyses of triphenylcarbalkoxymethylphosphonium salts in acetic acid–acetic anhydride and alcohols have indicated that three reactions can take place.[5,6] In the first, the evidence suggests a heterolytic cleavage *via* a transition state in which a partial positive charge is developing on the α-carbon of the alkoxy group. At the same time carbon dioxide and methylenetriphenylphosphorane are being generated. This mode of decomposition only occurs when a fairly stable carbonium ion can be generated.

The second reaction path involves attack by the hydroxylic solvent, SOH, on the acyl carbon atom of the salt. When SOH is an alcohol the transesterified product can often be isolated. When SOH is acetic acid–acetic anhydride further decomposition occurs to give triphenylmethylphosphonium bromide, carbon dioxide, and the alcohol derived from the alkoxy group of the salt. Usually the alcohol is converted to the acetate by the acetic anhydride.

The third mode of decomposition involves an SN2 attack on the α-carbon of the alkoxy group of the salt. This is generally a slow process when compared to the two reactions and in fact it has only been demonstrated for reactions where an alcohol is the solvent.

In the present study, the ^{12}C–^{13}C and ^{16}O–^{18}O isotope effects have been measured for the production of carbon dioxide during the acetolyses of triphenylcarbobenzhydryloxymethylphosphonium bromide (I), II, and triphenyl(carbo-*sec*-octyloxymethyl)phosphonium bromide (III). It was hoped that the data obtained from these studies would lead to a greater understanding of the reaction mechanisms involved and also that the data could be compared with calculated isotope effects obtained from various transition state models.

Experimental Section

Carbon-13 and Oxygen-18 Isotope Effects. A. **The solvolysis of triphenylcarbobenzhydryloxymethylphosphonium bromide** was carried out in glacial acetic acid–acetic anhydride (9:1, v:v) and followed kinetically by the rate of evolution of carbon dioxide. The apparatus used for the collection and measurement of evolved carbon dioxide is shown in Figure 1. The standard procedure was to place 35 ml of the acetic acid–acetic anhydride solvent in flask A and prepurified nitrogen gas, entering through the bulb above stopcock 1, was passed through the system for 20 min. After this time, stopcocks 1 and 4 were closed, and 3 was opened. By rotation about the two standard taper joints between flask A and condenser B, the flask was positioned in an oil bath, thermostated at 100.0 ± 0.2°. Thermal equilibrium was reached in about 20 min with the aid of a magnetic stirrer positioned below the flask. At this time, a solution of about 2.27 g of the phosphonium compound dissolved in 10 ml of the acetic acid–acetic anhydride solvent, was added through stopcock 1. Five milliliters of solvent was used to wash through any material adhering to the walls of the delivery bulb. During addition, the pressure was adjusted with the leveling bulb of the calibrated buret. Readings of the volume of evolved gas at constant pressure were taken as a function of time. The observed

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[1] Research support by the Atomic Energy Commission and the National Science Foundation under NSF GP-202 is gratefully acknowledged.

[2] Presented in part before the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P-137.

[3] (a) D. B. Denney, C. J. Rossi, and J. J. Vill, *J. Amer. Chem. Soc.*, 83, 3336 (1961); (b) D. B. Denney, C. J. Rossi, and J. J. Vill, *J. Org. Chem.*, 29, 1003 (1963).

[4] C. J. Rossi, Ph.D. Thesis, Rutgers, The State University, 1961.

[5] C. P. O'Farrell, Ph.D. Thesis, Rutgers, The State University, 1965.

[6] B. H. Garth, Ph.D. Thesis, Rutgers, The State University, 1966.

points of log ($V_\infty - V$) *vs.* time fall reasonably on a straight line. Only about 82% of the theoretical volume of carbon dioxide could be accounted for after ten half-lives.

At the end of the reaction period, the flask was lifted out of the bath by rotation about its joints and cooled in a Dry Ice–trichloroethylene bath. The system between stopcock 4 and the high-vacuum line was evacuated and the radiator trap, E, cooled in liquid nitrogen. Stopcock 4 was opened slightly so that the gas in the measuring system slowly passed through trap E. Carbon dioxide condensed in the trap and nitrogen passed through into the Toepler pump. The Toepler pump was used subsequently to draw the remaining gases slowly through the trap. After each pass through the Toepler pump, the noncondensable gases were discarded. When there appeared to be no remaining gas in the system, stopcocks 2, 3, and 4 were closed and flask A was warmed to room temperature. It was recooled, and the gases were removed by standard degassing techniques. The cycle was repeated three times.

Finally, stopcock 5 was closed and trap E warmed to room temperature in order to transfer the carbon dioxide through the Toepler pump to another container suitable for injection onto a vapor phase chromatographic column. To ensure complete removal of acetic acid or anhydride, the carbon dioxide was chromatographed on a 20% SF96 Silicone oil on Firebrick column at room temperature. Care was taken to ensure collection of the entire carbon dioxide sample. The samples were then analyzed with the aid of a Consolidated-Nier isotope ratio mass spectrometer.

B. Solvolysis of triphenylcarbooctyloxymethylphosphonium bromide proceeded at a much slower rate and was therefore carried out in sealed tubes. In a typical run to complete reaction, 20 ml of a 0.05 *M* solution of the phosphonium compound in the acetic acid–acetic anhydride solvent were added to a tube of about 40-ml volume fitted with a breakseal at one end and a standard tapered joint at the other. The contents were degassed on a high-vacuum line by standard techniques until no apparent gas remained, and then the tube was sealed and submerged in the thermostated bath at 100° for the required reaction period.

At the end of this period, the tube was cooled and opened under vacuum, and the contents were degassed with the aid of a Toepler pump. Complete degassing generally required about ten freeze-pump-thaw cycles. The carbon dioxide was then transferred to a calibrated buret for measurement before chromatographic purification. Recovered carbon dioxide amounted to 97.9 and 96.4% of theory for solvolysis of the *n*-octyl and 2-octyl compounds, after 16 and 43 days, respectively. Mass spectral analysis was carried out as described above.

In a typical run to only partial reaction, 50 ml of a 0.08 *M* solution of the phosphonium compound in the same solvent were added to a larger tube. r_c and r_p (see Discussion) were typically about 3.18 × 10^{-3} and 8.51 × 10^{-3}, respectively.

Attempted Oxygen Exchange. ^{18}O-Enriched carbon dioxide was prepared by shaking overnight natural carbon dioxide with ^{18}O-enriched water. After this reaction period, the contents of the flask were cooled in a Dry Ice bath; the carbon dioxide was Toepler pumped through a radiator trap cooled in Dry Ice in order to remove any water present. The gas was chromatographed on a Silicone oil column before use. Several attempted exchange experiments were carried out under varied conditions.

In one, 0.409 mmol of ^{18}O-enriched carbon dioxide was introduced into a 10-ml tube with breakseal containing 0.391 mmol of methyltriphenylphosphonium bromide dissolved in 3 ml of glacial acetic acid–acetic anhydride (9:1). The contents of the tube were degassed prior to the addition of the carbon dioxide. The tube was sealed and the contents were heated at 100.0° for 72 hr (*i.e.*, greater than $t_{1/2}$ for solvolysis of the *n*-octyl ester). Another reaction mixture containing 0.314 mmol of methyltriphenylphosphonium bromide, 0.329 mmol of carbon dioxide-^{18}O, and 3 ml of glacial acetic acid–acetic anhydride (9:1) was heated for 24 hr. At the end of this period the contents of each tube were cooled to Dry Ice temperature, and the tube was opened on a high-vacuum line. The carbon dioxide was Toepler pumped through a radiator trap cooled in Dry Ice into a gas buret. Several freeze-pump-thaw cycles were carried out to remove the bulk of the gas. The carbon dioxide was chromatographed on a Silicone oil column before mass spectrometric analysis. The analyses are shown as follows [(^{12}C^{16}O^{18}O)/(^{12}C^{16}O^{16}O), contact time (hr), % recovery, % exchange]: 0.015684 ± 0.000020, 24, 99, 0.9; 0.015642 ± 0.00007, 72, 97, 1.1. The initial (^{12}C^{16}O^{18}O)/(^{12}C^{16}O^{16}O) ratio was 0.015818 ± 0.000035.

In an other experiment, 0.318 mmol of ^{18}O-enriched carbon dioxide was added to 3 ml of glacial acetic acid–acetic anhydride (9:1) containing 0.312 mmol of methyltriphenylphosphonium bromide contained in a tube with breakseal having a volume of about 13 ml. The contents were shaken at 100.0° for 70 hr. The carbon dioxide was removed and purified as described above. Mass spectrometric analysis indicated that the (^{12}C^{16}O^{18}O)/(^{12}C^{16}O^{16}O) ratio was initially 0.015334 ± 0.000004 while in the recovered gas it was 0.015177 ± 0.000015 representing only about 1% exchange. Similar exchange experiments conducted in the absence of methyltriphenylphosphonium bromide produced essentially the same results.

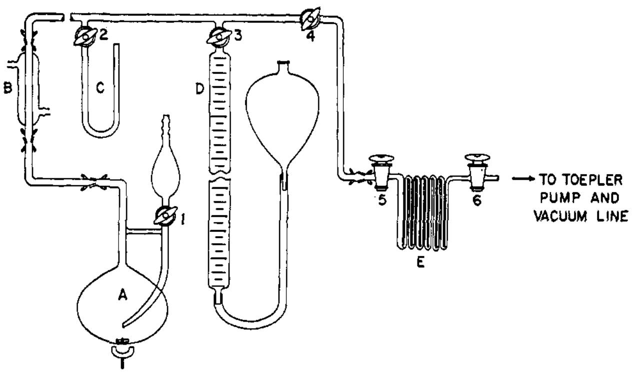


Figure 1. Gas collection system: A, reaction flask; B, condenser; C, manometer; D, gas buret; E, radiator trap.

Results

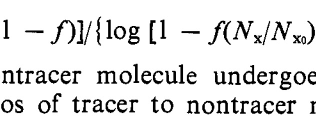
The carbon-13 and oxygen-18 kinetic isotope effects in the solvolysis of triphenylcarbalkoxymethylphosphonium bromides were determined on samples containing natural abundance quantities of these isotopes. With each of the three compounds I, II, and III, the

$(C_6H_5)_3P^+CH_2CO_2CH(C_6H_5)_2\ Br^-$

I

$(C_6H_5)_3P^+CH_2CO_2(CH_2)_7CH_3\ Br^-$

II



$(C_6H_5)_3P^+CH_2CO_2CH(C_6H_{13})(CH_3)\ Br^-$

III

isotopic content of carbon dioxide, evolved during complete solvolysis, was compared with that from a similar sample undergoing a known fraction of solvolysis. By using this method, the isotope effect, k/k', is given by eq 1[7] where f is the fraction of reaction

$$[\log(1 - f)]/\{\log[1 - f(N_x/N_{x0})]\} = k/k' \qquad (1)$$

that the nontracer molecule undergoes; N_x and N_{x0} are the ratios of tracer to nontracer molecules in the carbon dioxide at f fraction and complete reaction, respectively. The prime refers to the heavy isotope. Since the heavier isotope is present at only tracer levels, substitution of the experimentally observed total fraction of reaction for f introduces a very insignificant error in k/k'.

The quantity of carbon dioxide and hence the fraction of reaction during solvolysis of compounds II and III in acetic acid–acetic anhydride was measured after transfer of the gas to a calibrated manometric system. Acetic acid–acetic anhydride solvent appears to solvate carbon dioxide extremely well. Only after ten degassing cycles could one remove 97.9 and 96.4% of the theoretically expected carbon dioxide for compounds II and III, respectively. After only five de-

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(7) J. Bigeleisen, *Science*, 110, 14 (1949).

Table I. Corrected Mass Ratios and Isotope Effects in the Solvolysis of $(C_6H_5)_3P^+CH_2CO_2CH(C_6H_5)_2Br^-$

Sample	f	Corr 45/44	Corr 46/44		k_{12}/k_{13}[a]	k_{16}/k_{18}[a]
1A	1.00	0.011489	0.004164			
1B	1.00	0.011481	0.004222			
2A	1.00	0.011513	0.004168			
2B	1.00	0.011490	0.004211			
3A	1.00	0.011504	0.004188			
3B	1.00	0.011507	0.004179			
3C	1.00	0.011512	0.004190			
4	0.161	0.011043	0.004126		1.045	1.017
5	0.191	0.011044	0.004140		1.046	1.013
6	0.224	0.011067	0.004135		1.044	1.015
				Av	1.045 ± 0.001	1.015 ± 0.002

[a] Values calculated by use of eq 1.

Table II. Corrected Mass Ratios and Isotope Effects in the Solvolysis of $(C_6H_5)_3P^+CH_2CO_2(CH_2)_7CH_3Br^-$

Sample	f	Corr 45/44	Corr 46/44		k_{12}/k_{13}[a]	k_{16}/k_{18}[a]
1	1.00	0.011279	0.004121			
2	1.00	0.011257	0.004127			
3	1.00	0.011271	0.004128			
4	1.00	0.011263	0.004138			
5	0.170	0.011070	0.004128		1.020	1.000
6	0.215	0.011095	0.004134		1.018	0.998
7	0.168	0.011045	0.004135		1.022	0.998
				Av	1.020 ± 0.002	0.999 ± 0.001

[a] Values calculated by use of eq 1.

Table III. Corrected Mass Ratios and Isotope Effects in the Solvolysis of $(C_6H_5)_3P^+CH_2CO_2CH(CH_3)C_6H_{13}Br^-$

Sample	f	Corr 45/44	Corr 46/44		k_{12}/k_{13}[a]	k_{16}/k_{18}[a]
1	1.00	0.011393	0.004151			
2	1.00	0.011354	0.004146			
3	1.00	0.001373	0.004158			
4	0.178	0.011186	0.004152		1.0185	1.000
5	0.178	0.011196	0.004155		1.0176	1.002
6	0.178	0.011180	0.004137		1.0192	1.004
				Av	1.0184 ± 0.0006	1.002 ± 0.001

[a] Values calculated by use of eq 1.

gassing cycles slightly less than 75% of the gas was removed from the solvent and the space above. Since the rate of solvolysis of I is much greater than for either II or III, it was more convenient to follow gas evolution in the apparatus shown in Figure 1. It is not surprising that under these conditions only 82% of the theoretical gas appeared to be evolved after ten half-lives. At zero time the only gas in the system is nitrogen. As solvolysis proceeds the partial pressure of carbon dioxide increases and so the quantity of carbon dioxide dissolved in the solvent will gradually increase during the run in proportion to the extent of reaction. Reasonable first-order plots are obtained from the data derived by this method. In any case, almost complete removal of the carbon dioxide formed is realized by degassing.

The observed mass ratios and corresponding observed isotope effects (calculated with eq 1) are given in Tables I, II, and III. Before these effects were calculated the observed 45/44 ratios were corrected for mass resolution (ρ = 0.0001) and oxygen-17 abundance. Similarly the 46/(45 + 44) ratios were corrected for mass resolution and for the simultaneous presence of carbon-13 and oxygen-17. In order to minimize drift effects, each sample was bracketed by the measurement of these ratios for a standard sample of tank carbon dioxide and all readings were normalized to this sample. Mass ratios were generally taken three to four times and exhibited a deviation of about $\pm 5 \times 10^{-6}$. The deviation in the normalized ratio is then about $\pm 7.1 \times 10^{-6}$. Calculation of the isotope effect involves the ratio of two normalized ratios, N_x/N_{x_0}, and therefore its deviation is ±0.001. Since the gas buret was calibrated in tenths of a milliliter, the error in reading the volume of evolved carbon dioxide (about 15 ml after partial solvolysis) is extremely small. A greater uncertainty, perhaps 2% in f, may arise because of the way the extent of reaction was determined in runs of compound I. Errors in $(k/k') - 1$ generated by deviations in f and N_x/N_{x_0} have been treated previously by Bigeleisen and Allen.[8] For the errors assigned above, the relative error in $(k/k') - 1$ is expected to be about ±5%.

The calculated error is still quite small and of the order observed in Tables I, II, and III.

Discussion

As shown in Table IV the oxygen and carbon effects fall into two groups. A small carbon isotope effect is accompanied by the absence of an oxygen isotope effect for compounds II and III, while a large carbon isotope effect in the solvolysis of compound I is as-

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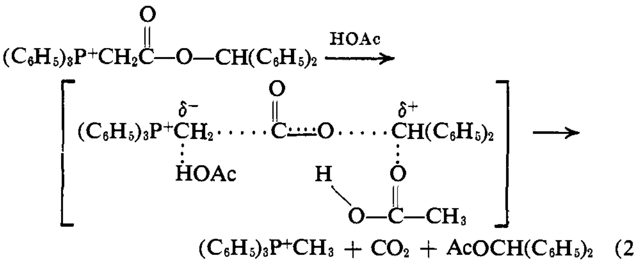
(8) J. Bigeleisen and T. L. Allen, *J. Chem. Phys.*, 19, 760 (1951).

Table IV. Summary of Isotope Effects in the Solvolysis of $(C_6H_5)_3P^+CH_2CO_2RBr^-$

R	k_{12}/k_{13}	k_{16}/k_{18}
$CH(C_6H_5)_2$	1.045 ± 0.001	1.015 ± 0.002
$(CH_2)_7CH_3$	1.020 ± 0.002	0.999 ± 0.001
$CH(CH_3)C_6H_{13}$	1.018 ± 0.001	1.002 ± 0.002

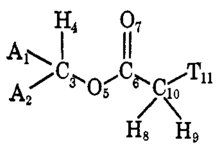
sociated with an oxygen effect about an order of magnitude larger than the error in its measurement. These facts taken together with the very large difference in solvolytic rates ($k_I/k_{II} \sim 95$, $k_I/k_{III} \sim 248$ at 103°)[5] suggest that the mechanism for solvolysis of II and III may be substantially different from that for the solvolysis of I.

In other solvolytic reactions the great difference in behavior between the benzhydryl and octyl groups lies in their abilities to form solvated carbonium ions. It would seem plausible that perhaps triphenylcarbobenzhydryloxymethylphosphonium bromide undergoes solvolysis by heterolytic cleavage of the oxygen–carbon bond with simultaneous rupture of the carbon–carbon bond to yield carbon dioxide, benzhydryl carbonium ion, and methylenetriphenylphosphorane (eq 2). Calculations were carried out to see if the isotope effect could indeed be used to support this mechanism.


(2)

Based on a program written by Schachtschneider, *et al.*,[9] to solve for vibrational frequencies from force constants, atomic masses, and geometry of polyatomic molecules, Wolfsberg[10] has written a program to calculate isotope effects in equilibria and rate processes. Wolfsberg and Stern have used this program to investigate the trend in isotope effect brought about by changes in force constants and geometry.[10] Their studies have shown that geometrical changes are generally of minor importance while alterations in the force field are the major contributing factor in producing an isotope effect.[10] In addition, the changes in force constants needed to reproduce experimental isotope effects have also been investigated and their mechanistic implications discussed.[10]

The Benzhydryl System. It has been shown that the calculation of isotope effects for a large molecule can be greatly simplified by neglecting atoms remote from the site of isotopic substitution.[10a,e] At or near room temperatures, insignifcant deviations are found in comparing the "cut-off" calculations with the more elaborate treatment. We have adopted this method by reducing triphenylcarbobenzhydryloxymethylphosphonium bromide (I) to an eleven-atom pseudomolecule IVa. Corresponding transition state models IVb and IVc were assumed.



IVa

$A_1 = A_2 =$ phenyl (mass 77)
T = triphenylphosphorus (mass 262)

The former, representing *simultaneous cleavage* at both the C_3–O_5 and C_6–C_{10} bonds, had both these bond lengths some 20% longer than in the corresponding reactant state. Furthermore, the O_5–C_6–O_7 angle was increased from 124 to 146° and the O_5–C_6 length was decreased by about 10% to reflect its intermediacy between ester and carbon dioxide. Other minor changes were: to decrease slightly the C_6–O_7 length, to allow the nonleaving groups around C_3 and C_{10} to approach planarity with the central atom, and finally to decrease the C_3–O_5–C_6 and O_5–C_6–C_{10} angles from its initial value to one midway between it and 90°.

Model IVc, representing *single* C_6–C_{10} *cleavage*, is a synthesis of the reactant state IVa and transition state IVb. Referring to structure IVa, all atoms in IVc left of the C_6–O_7 bond have the same geometry as in IVa while the atoms to the right of this bond have the geometry noted for IVb.

For each of these geometrical models, the *G* matrices for the various isotopically substituted reactants and transition states were calculated by choosing 36 internal coordinates for each.[10b] Force constants for each internal coordinate of the reactant were chosen from available values in the literature[9,11] and from these and the *G* matrices, frequencies and hence isotope effects were calculated.

In order to couple the breaking of the C_3–O_5 and the C_6–C_{10} bonds and thereby achieve simultaneous rupture of two bonds as in model IVb, a negative interaction force constant, f^*_{AB}, was introduced such that $f^*_A f^*_B - f^{*2}_{AB} \leq 0$, where f^*_A and f^*_B are the C_3–O_5 and C_6–C_{10} bond stretching force constants in the transition state, respectively. Matching of calculated and experimental isotope effects can be accomplished with this model by incorporating the following major changes in going from reactant to transition state: (a) setting $f^*_A/f_A \sim 0.5$ and $f^*_B/f_B \sim {}^1/_{16}$ and (b) reducing the bending force constants associated with O_5 some 20 to 30% while those associated with C_6 some 50 to 90%. The results are shown in Table V.

The carbon–oxygen stretching force constant of carbon dioxide is considerably greater than the reactant O_5–C_6 and O_7–C_6 stretching force constants. For this reason it was anticipated that these force constants would be greater in the transition state than

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(9) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

(10) (a) M. Wolfsberg and M. Stern, *Pure. Appl. Chem.*, 8, 225 (1964); we thank Dr. Wolfsberg for making this program available to us; (b) M. Wolfsberg and M. Stern, *ibid.*, **8**, 325 (1964); (c) M. J. Goldstein and G. L. Thayer, Jr., *J. Amer. Chem. Soc.*, **87**, 1933 (1965); (e) S. Seltzer and S. M. Mylonakis, *ibid.*, **89**, 6584 (1967); (e) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, **45**, 4105 (1966).

(11) (a) See footnotes in Table V for a complete tabulation of the force constants used; (b) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p 193; (c) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 175; (d) D. A. Long and R. B. Gravenor, *Spectrochim. Acta*, **19**, 961 (1963); (e) S. Bratoz and S. Besnainou, *J. Chem. Phys.*, **34**, 1142 (1961); (f) H. Siebert, *Z. Anorg. Allgem. Chem.*, **271**, 65 (1952); (g) J. C. Evans and J. Overend, *Spectrochim. Acta*, 19, 701 (1963); (h) E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **9**, 319 (1941).

in the reactant. Adjustment of these two constants in this direction, however, appears to make impossible the fitting of calculated with the experimental C^{13} isotope effect.

A transition state where only the C_6–C_{10} bond ruptures was also tested. Here using model IVc, f^*_B was set equal to zero to achieve bond breaking. Good correspondence with experimental results can be obtained in two different ways: (a) by reducing the C_3–O_5 stretching force constant to about half its original value, by increasing the O_5–C_6 constant about 10%, and by reducing the bending force constants involving O_5 some 15% but those involving C_6 some 80%, or (b) by reducing the carbonyl stretching force constant by about 20%, the bending force constants associated with C_6 about 50%, and the bending force constants pertaining to O_5 by about 15%.[12] These results are also shown in Table V.

More exact fitting of calculated with experimental results can be obtained by further small adjustments of force constants but, in our opinion, would be not worthwhile. Undoubtedly, other force fields, differing in only a minor way from those shown in Table V, might also lead to the same calculated kinetic isotope effects but the mechanistic conclusions derived from these would be the same. The possibility that more diverse force fields, than those shown in Table V, can be used to successfully reproduce the experimental observations, of course, always exists.

The observation of a large C^{13} isotope effect in this decarboxylation makes it inconceivable that the C_6–C_{10} bond does not rupture in the slow step[13] and therefore a transition state where only the C_3–O_5 and not the C_6–C_{10} bond breaks was not considered in detail. Although models IVb and IVc differ in the relative timing of carbon–carbon to carbon–oxygen bond breaking, *they are in agreement that carbon–carbon bond stretching is more advanced than carbon–oxygen bond extension.* Model IVb, because of its coupled motion, has both of these bonds stretching or contracting at the same time. In the transition state they extend simultaneously. Model IVc, on the other hand, allows these two bonds to act independently of each other. Therefore in going from reactant to transition state the carbon–carbon bond can be stretching to break while the carbon–oxygen can be contracting (or stretching) with a weaker force constant than in the reactant. Matching of calculated and experimental isotope effects in this instance cannot differentiate between simultaneous and stepwise two-bond rupture. Nor does it appear that the isotope-effect dependence on the temperature can be used to answer this question. The calculations for models IVb and IVc indicate only very small differences between the two, at temperatures where the reaction can be studied conveniently.

The *n*-Octyl and 2-Octyl Systems. The most striking observation is the absence of a significant oxygen isotope effect for either octyl ester during solvolysis while in the benzhydryl system this isotope effect is 1.015. The absence of an oxygen-18 isotope effect in the carbon dioxide product could have been the result of rapid and complete oxygen exchange between carbon dioxide and the solvent; however, ^{18}O-enriched carbon dioxide, in contact with the solvent under the conditions that it is formed, exchanges only about 1% of its oxygen atoms during a reaction time greater than the half-life for solvolysis of triphenylcarbooctyloxymethylphosphonium bromide. *A priori*, one might conclude that in the octyl systems only the carbon–carbon bond ruptures in the slow step of the process to form carbon dioxide. This mechanism, however, cannot account for the solvolysis rate ratio, $k_{II}/k_{III} \sim 2.6$. A value of unity or smaller might have been expected for just carbon–carbon cleavage.

A more salient difference is in their mode of cleavage. *Product studies*[5,6] *have shown that compound I solvolyzes with benzhydryl–oxygen cleavage while II and III with*

Table V. Comparison of Calculated and Experimental Carbon and Oxygen Isotope Effects in the Solvolysis Triphenylcarbobenzhydryloxymethylphosphonium Bromide at 100°

	Calculated			
	Model IVb[a]	Model IVc		Experimental
k_{12}/k_{13}	1.043	1.042[b]	1.048[c]	1.045 ± 0.001
k_{16}/k_{18} (oxo)	1.010	1.011[b]	1.015[c]	
k_{16}/k_{18} (oxy)	1.024	1.018[b]	1.010[c]	
k_{16}/k_{18} (av)	1.017	1.015[b]	1.013[c]	1.015 ± 0.002

[a] Using the numbering system in IVa, the following is the set of force constants used to calculate the above kinetic isotope effects. Reactant (units are mdyn/Å for stretches, mdyn-Å for bends and torsions): $f_{1-3} = f_{2-3} = 4.39, f_{3-4} = 4.62, f_{3-5} = 5.28, f_{5-6} = 5.50, f_{6-7} = 10.3, f_{6-10} = 4.85, f_{8-10} = f_{9-10} = 4.52, f_{10-11} = 3.03, f_{1.3.2} = 0.90, f_{1.3.4} = f_{2.3.4} = f_{6.10.8} = f_{6.10.9} = 0.667, f_{1.3.5} = f_{2.3.5} = f_{5.6.7} = f_{5.6.10} = 1.0, f_{4.3.5} = 1.11, f_{3,5.6} = 1.27, f_{7.6.10} = 1.2, f_{6.10.11} = 0.450, f_{8.10.11} = f_{9.10.11} = 0.60, f_{8.10.9} = 0.55, f_{1.3.5.6} = f_{2,3.5.6} = f_{4.3.5.6} = f_{3.5.6.7} = f_{7.6.10.8} = f_{7.6,10.9} = f_{7.6,10,11} = 0.015$ (torsion), $f_{5.6.7,10} = f_{10.6.5.7} = 0.06$ (out-of-plane wag of atoms 5 and 10, respectively), $f_{7.6.5.10} = 0.18$ (out-of-plane wag for atom 7). Force constants for the transition state were the same as for the reactant except for: $f^*_{1-3} = f^*_{2-3} = 5.33, f^*_{3-4} = 4.70, f^*_{3-5} = 2.50, f^*_{6-10} = 0.30, f^*_{8-10} = f^*_{9-10} = 4.60, f^*_{1.3.2} = 1.12, f^*_{1.3.4} = f^*_{2.3.4} = 0.65, f^*_{1.3.5} = f^*_{2,3.5} = 0.80, f^*_{4.3.5} = f^*_{3.5.6} = 0.90, f^*_{5.6.7} = f^*_{5.6.10} = 0.60, f^*_{7.6.10} = f^*_{6.10.8} = f^*_{6.10.9} = 0.10, f^*_{6,10.11} = 0.30, f^*_{8.10.11} = f^*_{9.10.11} = 0.55$, all $f^*_{\text{torsions}} = 0.001, f^*_{7.6.5.10} = f^*_{5.6,7.10} = 0.06, f^*_{10.6.5,7} = 0.03, f^*_{8.10.9} = 0.47, f^*_{3-5 \text{ interaction with } 6-10} = -0.86603$, [b] Reactant force constants are the same as shown above. Transition state force constants are the same as for the reactant except: $f^*_{3-5} = 2.8, f^*_{5-6} = 6.0, f^*_{6-10} = 0.0, f^*_{8-10} = f^*_{9-10} = 4.60, f^*_{10-11} = 3.30, f^*_{1.3,5} = f^*_{2.3.5} = 0.90, f^*_{4.3.5} = 1.0, f^*_{3.5.6} = 1.10, f^*_{5.6,7} = 0.7, f^*_{5,6.10} = 0.2, f^*_{7.6.10} = 0.30, f^*_{6,10.8} = f^*_{6.10,9} = 0.1, f^*_{6.10.11} = 0.08, f^*_{8.10.11} = f^*_{9.10,11} = 0.55, f^*_{7.6.10.8} = f^*_{7.6,10.9} = f^*_{7.6.10.11} = 0.001, f^*_{3.5.6.7} = 0.03, f^*_{8.10.9} = 0.47, f^*_{7.6.5,10} = f^*_{5.6,7,10} = 0.06, f^*_{10,6,5,7} = 0.003$. [c] Reactant force constants are the same as shown above. Transition state force constants are the same as for the reactant except: $f^*_{6-7} = 8.7, f^*_{6-10} = 0.0, f^*_{8-10} = f^*_{9-10} = 4.60, f^*_{10-11} = 3.30, f^*_{5,6,7} = f^*_{1.3.5} = f^*_{2.3.5} = 0.85, f^*_{4.3.5} = 0.90, f^*_{3.5.6} = 0.80, f^*_{5,6.10} = 0.5, f^*_{7,6,10} = 0.6, f^*_{6.10.8} = f_{6,10.9} = 0.4, f^*_{6.10.11} = 0.2, f^*_{8.10,11} = f^*_{9,10.11} = 0.55, f^*_{7.6.10.8} = f^*_{7.6.10.11} = 0.001, f^*_{8,10.9} = 0.47, f^*_{7.6,5.10} = f^*_{5.6.7.10} = 0.06, f^*_{10,6.5.7} = 0.003$.

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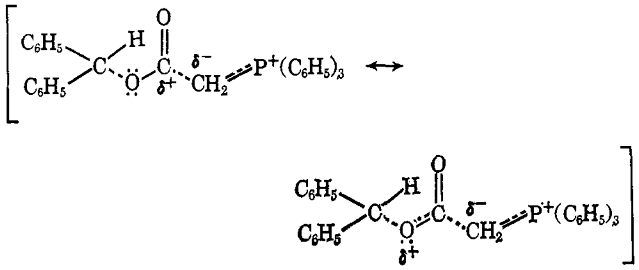
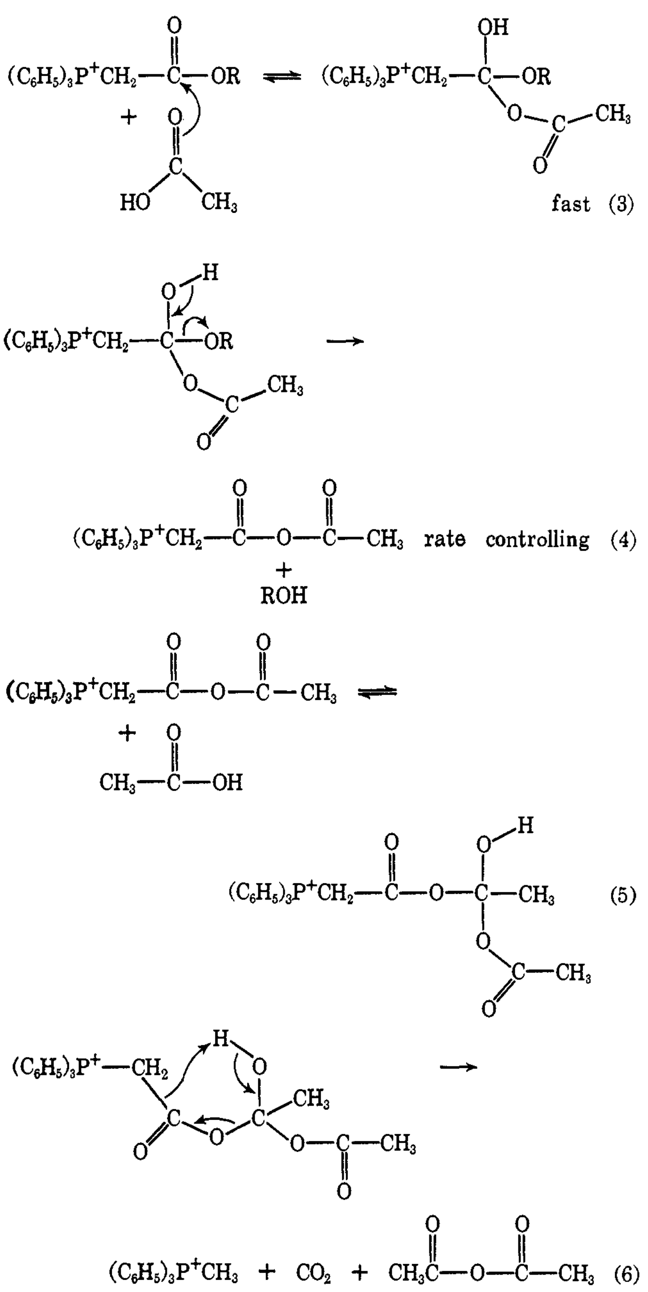
[12] The former force field of single bond rupture might correspond to charge delocalization in the transition state.



Although reasonable fitting can be obtained with the latter model there appears to be no good mechanistic justification for it.

[13] See, *e.g.*, S. Seltzer, G. Hamilton, and F. H. Westheimer, *J. Amer. Chem. Soc.*, **81**, 4018 (1959).

octyloxy-carbon cleavage. Any proposed mechanism for solvolysis of triphenylcarbooctyloxymethylphosphonium bromide, therefore, *requires* one of the oxygen atoms of the carbon dioxide formed to come from the acetic acid–acetic anhydride solvent. Moreover, the absence of an oxygen isotope effect probably indicates that the eventual scission of this new oxygen atom from its parent acetyl group not be rate controlling. A mechanism which incorporates these features is given in eq 3–7, where R = *n*-octyl or 2-octyl.



$$ROH + (CH_3CO)_2O \longrightarrow ROCOCH_3 + CH_3CO_2H \qquad (7)$$

Assuming that the loss of the alcohol (eq 4) is rate controlling, the observed isotope effects are determined by the preequilibrium isotope effects (eq 3) and the kinetic isotope effects in eq 4.

If reaction 4 is slow compared to the steps following it, then

$$\frac{d(^{12}CO_2)}{d(^{13}CO_2)} = \frac{k_{12}K_{12}(E_{12})(A)}{k_{13}K_{13}(E_{13})(A)} \qquad (8)$$

where (A) is the concentration of acetic acid and (E_{12}) and (E_{13}) refer to the corresponding concentrations of carbonyl-^{12}C and carbonyl-^{13}C octyl esters at any time. K_{12} and K_{13} are the isotopic equilibrium constants for formation of the tetrahedral intermediate in reaction 3 when carbon-12 or -13 is in the carbonyl group, while k_{12} and k_{13} are the corresponding isotopic first-order rate constants for reaction 4. This easily leads to $(k_{12}/k_{13})_{obsd} = (k_{12}K_{12})/(k_{13}K_{13})$. The observed oxygen-18 isotope effect, on the other hand, is the mean of separate fractionation factors for each oxygen atom. The effect originating from the carbonyl oxygen of the ester is given by

$$\frac{d(C^{16}O^{16}O)_E}{d(C^{16}O^{18}O)_E} = \frac{k_{16}K_{16}(E_{16})(A)}{k_{18}K_{18}(E_{18})(A)} \qquad (9)$$

where the subscripts refer to the oxygen-16 and -18 originally in the carbonyl group of the ester. Similarly, this portion of the isotope effect is given by $(k_{16}K_{16})/(k_{18}K_{18})$.

The other oxygen atom of carbon dioxide is derived from acetic acid so that

$$\frac{d(C^{16}O^{16}O)_A}{d(C^{18}O^{16}O)_A} = \frac{k_{16}'K_{16}'(E)(A_{16})}{k_{18}'K_{18}'(E)(A_{18})} \qquad (10)$$

Here the subscripts refer to the two oxygen isotopes originally in the carbonyl group of acetic acid. Subscripts, denoting the isotopic species of ester ethereal oxygen, have been omitted since the isotopic oxygen abundance in carbon dioxide would appear to be independent of the abundance at the ethereal oxygen. Integration and substitution (see Appendix) leads to eq 11 where N_f and N_∞ are the ^{18}O–^{16}O ratios in

$$\frac{N_f}{N_\infty} = \left(\frac{1 - (1 - fr_p)^{k_H/k_L}}{fr_p}\right)\left(\frac{r_c}{1 - (1 - r_c)^{k_H/k_L}}\right) \qquad (11)$$

carbon dioxide at *f*, fraction of reaction, and at infinity, respectively. The initial ratios of the concentration of phosphonium ester to acetic acid are given by r_p and r_c where the subscripts refer to the partial and complete reactions. The pseudo-first-order rate constant ratio, k_H/k_L, equals $(k_{18}'K_{18}')/(k_{16}'K_{16}')$. Since the concentration of acetic acid is so much greater than substrate, it is easily seen that the difference in isotopic abundance of the product at low (N_f) and complete (N_∞) conversion will be very small even though k_H/k_L may differ significantly from unity. It remains then to calculate equilibrium and kinetic efforts for reactions 3 and 4 for both isotopes.

A similar problem has been treated previously by Bigeleisen[14] in his theoretical calculation to reproduce experimental carbon-14 isotope effects obtained by Stevens and coworkers[15] in the saponification of ethyl benzoate. Although the experimental isotope effects were shown later to be too high,[16] the proposal[14] that the observed effect results from the product of an inverse equilibrium isotope effect, expected in the reversible addition of hydroxide ion to the ester, and a normal kinetic isotope effect, in the loss of ethoxide, still appears to be justified.

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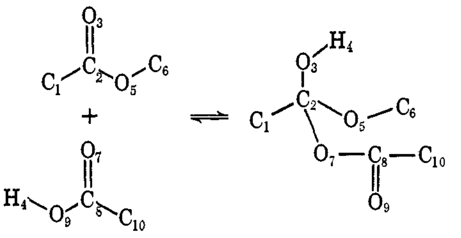
(14) J. Bigeleisen, *J. Phys. Chem.*, 56, 823 (1952).

(15) W. H. Stevens, J. M. Pepper, and M. Lounsbury, *J. Chem. Phys.*, 20, 192 (1952).

(16) G. A. Ropp and V. F. Raaen, *ibid.*, 22, 1223 (1954); see especially footnote 7 in this paper.

As a model for reaction in eq 3, the pseudomolecular equilibrium in eq 12 was considered. A "cut-off" procedure was used in order to simplify the calculation of equilibrium constants for isotopic substitution at different sites. Aside from the usual masses of the atoms, the terminal carbon atoms, C_1, C_6, and C_{10} of the natural compound were assigned masses of 14, 14, and 15, respectively, to take account of the protons bonded to these atoms. Here too, bond lengths and angles are in accord with accepted values.[17] By using 33 internal coordinates to describe fully the vibrations of the ester-acid adduct and 13 each to describe those of the pseudo ester and pseudo acetic acid, the equilibrium isotope effects, shown in Table VI, were calculated. The force constants for these calculations are shown in the footnotes to the table.[11]



(12)

Table VI. Calculated Equilibrium Isotope Effects at 100° [a]

$$\frac{K_L}{{}_nK_m} = \frac{(\text{adduct})_L/(\text{adduct})_H}{[(\text{ester})_L/(\text{ester})_H][(\text{acetic acid})_L/(\text{acetic acid})_H]}$$

Atom	m	n	$K_L/{}_nK_m$
C	13	2	0.9817[b]
O	18	3	0.9912[b]
O	18	5	0.9987[b]
O	18	7	0.9733[b]
C	13	8	1.0007[b]
O	18	9	1.0104[b]

[a] m is the mass of the heavy isotope and n is the position of the isotope designated in eq 12. The subscripts L and H refer to light, and heavy, respectively. [b] By using the numbering system in eq 12 the following is a set of force constants used for the calculation of equilibrium isotope effects (units are as in Table V, footnote *a*). Pseudo ester: $f_{1-2} = 4.85$, $f_{2-3} = 10.3$, $f_{2-5} = 5.5$, $f_{5-6} = 5.28$, $f_{1.2,3} = f_{3,2.5} = 1.20$, $f_{1,2.5} = 1.0$, $f_{2.5.6} = 1.27$, $f_{1.2.5.6} = f_{3.2.5.6} = 0.015$ (torsion), $f_{1,2.3.5} = f_{5,2.1.3} = 0.06$ (1 and 5 out-of-plane wag), $f_{3.2.1,5} = 0.18$ (3 out-of-plane wag). Pseudo acetic acid: $f_{10-8} = 4.85$, $f_{7-8} = 10.3$, $f_{8-9} = 5.5$, $f_{4-9} = 7.69$, $f_{7.8.10} = f_{7.8.9} = f_{8.9,4} = 1.2$, $f_{10.8.9} = 1.0$, $f_{10.8.7.9} = f_{9.8.7.10} = 0.06$, $f_{7.8.9.10} = 0.18$, $f_{10.8.9.4} = f_{7.8.9.4} = 0.015$. Pseudo ester-acetic acid adduct: $f_{1-2} = 4.50$, $f_{2-3} = 5.28$, $f_{3-4} = 7.69$, $f_{2-5} = f_{5-6} = f_{2-7} = 5.28$, $f_{7-8} = 5.50$, $f_{8-9} = 10.3$, $f_{8-10} = 4.85$, $f_{1.2.3} = f_{1.2.5} = f_{1.2.7} = f_{7.8,10} = 1.0$, $f_{2,3.4} = f_{3.2.5} = f_{3.2.7} = f_{5.2.7} = f_{7.8.9} = f_{9.8,10} = 1.2$, $f_{2.5.6} = f_{2.7.8} = 1.27$, $f_{1.2.5.6} = f_{1.2.3.4} = f_{2.7.8.10} = f_{2.7.8.9} = f_{6.5.2.7} = f_{4.3.2.7} = 0.025$, $f_{1.2.7.8} = f_{3.2.7.8} = f_{5.2.7.8} = 0.016$, $f_{7.8.9.10} = f_{10.8,9.7} = 0.06$ (7 and 10 out-of-plane wag), $f_{9.8.7.10} = 0.18$ (9 out-of-plane wag).

These calculations predict that the heavy isotopes of oxygen and carbon, in atom positions 3 and 2, respectively, concentrate in the ester–acid adduct rather than in the initial pseudo ester compound. It should be recalled that these are two of the three atoms to be found in the carbon dioxide product. The abundance levels of these two isotopes in the product will then vary with extent of solvolysis and will be responsible for a portion of the observed isotope effects. By this reaction scheme, the third atom, oxygen at position 7, is supplied by the carbonyl group of acetic acid. Although, a substantial enrichment of oxygen-18 is anticipated for this position in the ester–acid adduct when compared to acetic acid, the oxygen-18 abundance for this position can be shown by eq 11 not to vary appreciably with the extent of solvolysis. Since the concentration of acetic acid is 300 to 800 times the concentration of phosphonium ester, the oxygen isotopic ratio of acetic acid is essentially unaltered by the relatively small loss of molecules of higher oxygen-18 content to the ester to form the ester-acid adduct. Finally, only a small equilibrium fractionation effect is calculated for the oxygen bonded to the octyl groups (atom position 5).

Kinetic isotope effects were also calculated for the reaction shown in eq 4. The ester-acid adduct was considered to be the reactant, and the G matrices and force field used for this pseudointermediate, in the calculation of equilibrium constants, were also used for the reactant in the calculation of kinetic effects. The basic geometry of the transition state was the same as that in the reactant except for a few changes. To take account of C_2–O_5 and O_3–H_4 cleavage (see eq 12), these bond lengths were arbitrarily increased 5 and 10%, respectively. Along with this change is the probable development of a C_2–O_3 double bond and the conversion of the C_2–O_7 bond to an anhydride linkage. Both these bond lengths were reduced about 7%.

In the conversion of a carbonyl carbon to a tetrahedral atom and in the absence of strong field effects the initial approach of the attacking nucleophile is probably along a line perpendicular to the plane formed by the carbon and the three atoms bonded to it. Deviations from this approach might result if an irregular tetrahedral configuration is eventually formed. The reverse reaction, here the rupture of the C_2–O_5 bond (eq 4), would be expected to be accompanied by a decrease in the angles made by O_5–C_2– and each of the other three atoms bonded to C_2. These three angles were all reduced to about 100° in the transition state. In addition, the angles formed by any of the two of the three remaining groups bonded to C_2 were increased, to coincide with its approach toward sp^2 hybridization.

The force field for the transition state was essentially the same as that for the reactant except for a few changes. Of greatest importance is the reduction of the C_2–O_5 stretching force constant to zero in order to obtain a transition state corresponding to C_2–O_5 bond rupture. In addition, the four bending force constants associated with O_5 were reduced to one-fourth their reactant state values in order to achieve the kinetic effects shown in Table VII.

Assuming that the mechanism of solvolysis for both octyl esters is that given in eq 3–7, the observed ^{13}C and ^{18}O effects are those derived from the products of the kinetic effects in eq 4 and the equilibrium effects in eq 3. The first line of Table VIII compares the calculated and experimental carbon-13 effects. The ^{18}O effect, as already noted, is an average of the effects when heavy oxygen is substituted at O_3 and then at O_7. Each of these in turn is determined by the product of the equilibrium and kinetic effects and is shown as the second and third entries in the "theoretical" column of

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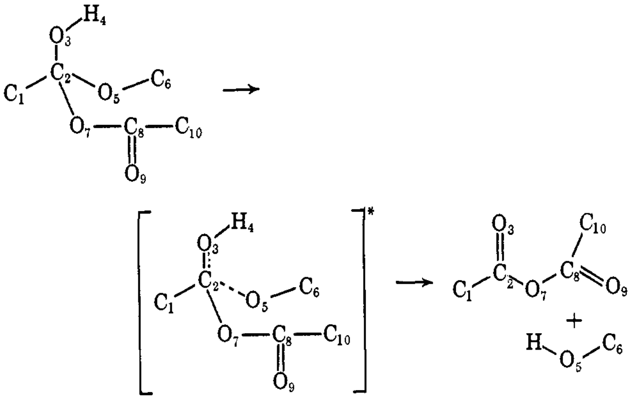
(17) "Tables of Interatomic Distances and Configuration of Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, p M151; Supplement 1956–1959, Special Publication No. 18, The Chemical Society, London, 1965, p M82S.

Table VII. Calculated Kinetic Carbon and Oxygen Isotope Effects at 100° [a]

Atom no.[b]	Isotope[b]	k_L/k_H[c]
2	^{13}C	1.040
3	^{16}O	1.0034
7	^{18}O	1.0050

[a] These effects have been calculated for the pseudomolecular reaction



which serves as a model for the reaction in eq 4. [b] Refers to the numbering in *a*. [c] With the numbering in footnote *a*, the following is the set of force constants used to obtain the calculated kinetic effects shown above. Reactant: these are identical with the force constants shown in Table VI, footnote *b* for the pseudo ester–acetic acid adduct. Transition state force constants are the same as for the reactant except $f^*_{2-5} = 0.0$, $f^*_{1,2,5} = 0.25$, $f^*_{3,2,5} = f^*_{2,5,6} = f^*_{5,2,7} = 0.3$.

Table VIII. Experimental and Calculated Carbon and Oxygen Isotope Effects in the Solvolysis of Phosphonium Octyl Esters at 100°

	Atom no.	Theoret	Expected	Obsd	
				2-Octyl	*n*-Octyl
k_{12}/k_{13}	2	1.021	1.021	1.018 ± 0.001	1.020 ± 0.002
k_{16}/k_{18}	3	0.9946	0.9946		
k_{16}/k_{18}	7	0.9782	1.0000[a]		
k_{16}/k_{18}	Av		0.9973	1.002 ± 0.001	0.999 ± 0.001

[a] Theoretical and expected isotope effects differ for atom no. 7 because r_p and r_c (see eq 11) are both very small.

Table VIII. "Theoretical" and "expected" isotope effects at O_7 differ because this oxygen atom is derived from the solvent. If the "theoretical" isotope effect ($k_{16}/k_{17} = 0.9782$) is substituted into eq 11 with r_c and r_p equal to 3.18×10^{-3} and 8.51×10^{-3}, respectively (see Experimental Section), and f equals about 0.2, the expected ratio N_f/N_∞ equals 1.0000. It is easily seen from eq 1 that the over-all isotope effect at O_7 would then be 1.0000 as shown in the "expected" column of Table VIII. The average effect for both oxygen atoms (last entry in that column) is quite close to both observed oxygen isotope effects. Further calculations to obtain closer fitting between experimental and calculated results seems possible but appears to us not worthwhile. The good correspondence between the experimental and calculated results then, lends support to the mechanism indicated in eq 3–7.

In summary, the process of fitting calculated and observed isotope effects leads to a solution of reactant and transition-state force fields. Since there are generally many more adjustable force constants than observed isotope effects, the force fields that are obtained are possible but generally not unique solutions. The strength of the method lies in its ability to reject particular transition states. Just as in a study of kinetic, stereochemical, or electronic effects of a reaction, isotope effects and exact calculations can only support, but not prove, a mechanism. Thus it is entirely possible that the experimental data might be accommodated by variations of the mechanisms presented above.

Acknowledgment. The authors would like to express their great appreciation to Drs. Max Wolfsberg and Marvin Stern for discussions concerned with the calculation of isotope effects. They would also like to thank Mr. Ted Middleton for mass spectral analysis and Mr. Stamatios Mylonakis for ^{18}O exchange experiments.

Appendix

Let $x = (C^{16}O^{16}O)_A$, $y = (C^{18}O^{16}O)_A$, and $k_L/k_H = k'_{16}K'_{16}/k'_{18}K'_{18}$. Substitution of these quantities into eq 10 and integration leads to eq 13 where the zero subscript refers to initial concentrations. Since the

$$\ln \frac{(A_{16})_0 - x}{(A_{16})_0} = \frac{k_L}{k_H} \ln \frac{(A_{18})_0 - y}{(A_{18})_0} \qquad (13)$$

heavy isotope is present in only tracer concentrations the fraction of reaction, f, can be defined as x_f/E_0 with negligible error. If $y_f/x_f = N_f$, $y_\infty/x_\infty = N_\infty$, and $(A_{18})_0/(A_{16})_0 = R_{A_0}$, eq 13 is transformed into (14) by substitution of these quantities. Since the experimental conditions were slightly different in partial (p) and complete (c) solvolysis runs, we must define r as the initial ratio of concentration of ester to light acetic acid so that

$$\ln\left(1 - \frac{fE_0}{(A_{16})_0}\right) = \frac{k_L}{k_H} \ln\left(1 - \frac{fE_0N_f}{(A_{16})_0R_{A_0}}\right) \qquad (14)$$

$$r_p = \left(\frac{E_0}{(A_{16})_0}\right)_p$$

and

$$r_c = \left(\frac{E_0}{(A_{16})_0}\right)_c$$

Substitution of these quantities into eq 14 leads to eq 15

$$\ln(1 - fr_p) = \frac{k_L}{k_H} \ln\left(1 - fr_p\frac{N_f}{R_{A_0}}\right) \qquad (15)$$

Similarly, at $f = 1.0$, eq 13 can be written as

$$\ln\left(1 - \frac{x_\infty}{(A_{16})_0}\right) = \frac{k_L}{k_H} \ln\left(1 - \frac{y_\infty}{(A_{18})_0}\right) \qquad (16)$$

which upon substitution of the quantities defined above leads to

$$\ln(1 - r_c) = \frac{k_L}{k_H} \ln\left(1 - r_c\frac{N_\infty}{R_{A_0}}\right) \qquad (17)$$

Rearrangement of eq 15 and 17 yields eq 18 and 19, respectively.

$$\frac{N_f}{R_{A_0}} = \frac{1 - (1 - fr_p)^{k_H/k_L}}{fr_p} \qquad (18)$$

$$\frac{N_\infty}{R_{A_0}} = \frac{1 - (1 - r_c)^{k_H/k_L}}{r_c} \qquad (19)$$

If eq 18 is divided by eq 19, eq 11 is obtained.