

residue was stirred with hexane and filtered. The solid (6.75 g) was recrystallized from hexane to give 5.6 g (28% conversion of anion) of 1-chloro-2,2,4,4-tetraphenylbutane, mp 121–122°.

*Anal.* Calcd for  $C_{28}H_{28}Cl$ : Cl, 8.93. Found: Cl, 9.06.

The hexane filtrate was evaporated and the residual oil was distilled at 2 mm to give 5.2 g (31% recovery) of diphenylmethane, bp 89–96°. The still pot residue was crystallized in hexane and recrystallized from methanol to give 5.1 g (28% conversion) of 1,1,3,3-tetraphenylpropane, mp 139.5–141.5°. Diphenylethylene was detected in the combined mother liquors by gas chromatography (estimated 0.95 g, 5.3% conversion).

**Reaction of Potassium Diphenylmethide with 1,1-Diphenylethylene.**—To a solution of 0.05 mol of potassium diphenylmethide in 120 ml of liquid ammonia was added an ethereal solution of 9 g (0.05 mol) of 1,1-diphenylethylene. The dark red solution was stirred for 20 min and 3 g of ammonium chloride was added. The ammonia was evaporated and the residue was stirred with ether and water. The ethereal solution was separated, washed, dried, and evaporated to give 17.4 g of solid. Recrystallization from ethanol and hexane gave 9 g (52%) of tetraphenylpropane, mp 139–140°. Another 5.4 g of lower melting product was obtained from the mother liquor. In another experiment, 5.4 g (0.03 mol) of 1,1-diphenylethylene in ether was added to 0.03 mol of potassium diphenylmethide, and the deep red solution was stirred for 30 min. An ethereal solution of 2.6 g (0.03 mol) of methylene chloride was added. The color was slowly (25 min) discharged. Work-up as above gave 7.4 g (62%) of tetraphenylchlorobutane, 2.3 g (22%) of tetraphenylpropane, and 15% each of diphenylmethane and diphenylethylene.

**Reaction of 1,1-Diphenyl-1-propene with Potassium Amide.**—To a solution of 0.025 mol of potassium amide in 100 ml of liquid ammonia was added an ethereal solution of 4.85 g (0.025 mol) of

1,1-diphenyl-1-propene. The ammonia was replaced with ether, and the deep red solution was poured onto Dry Ice. Water was added and the aqueous layer was separated and acidified. The solid was recrystallized from carbon tetrachloride to give 3 g (50%) of 4,4-diphenyl-3-butenic acid, mp and mmp 118–119°.<sup>9</sup>

**Reaction of Potassium Triphenylmethide with Methylene Chloride.**—To a solution of 0.025 mol of potassium triphenylmethide, prepared from 0.025 mol of potassium amide and 6.1 g (0.025 mol) of triphenylmethane in liquid ammonia, was added 2.4 g (0.028 mol) of methylene chloride. The color was not discharged after 40 min. Ammonium chloride was added to discharge the color and the ammonia was evaporated. The residue was stirred with ether and water and the ethereal layer was separated, dried over magnesium sulfate, and evaporated. The residue was recrystallized from methylene chloride-ethanol to give 3.8 g (52%) of 1-chloro-2,2,2-triphenylethane, mp 99–100°. The experiment was repeated, except that after the methylene chloride had been added and the solution stirred for 20 min an ammoniacal solution of 0.025 mol of potassium amide was added, and the mixture was stirred until the ammonia had evaporated (about 1.5 hr). Work-up as above afforded only triphenylethyl chloride (53%), and triphenylethylene could not be detected.

**Registry No.** —1, 101-81-5; 1', 10060-17-0; 3, 36171-50-3; 4, 40139-28-4; 5, 530-48-3; methylene chloride, 75-09-2; 1,1-diphenyl-1-propene, 778-66-5; potassium amide, 17242-52-3; 4,4-diphenyl-3-butenic acid, 7498-88-6; potassium triphenylmethide, 1528-27-4; 1-chloro-2,2,2-triphenylethane, 33885-01-7.

(9) W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Amer. Chem. Soc.*, **69**, 74 (1947).

## Kinetic Isotope Effects in the Oxidation of Alcohols by Silver Carbonate

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The kinetic isotope effect resulting from the silver carbonate oxidation of a variety of alcohols has been determined by a convenient double labeling technique which may be utilized for similar determinations in other systems. The method is especially suitable to systems where reproducible direct kinetic measurements are not possible. The theory strengths and limitations of the method are discussed and its validity is experimentally verified.

The importance of kinetic isotope effects in the study of organic reaction mechanisms is well known and has been extensively reviewed.<sup>1</sup> Frequently the mere existence or absence of a kinetic isotope effect is a sufficient clue for the differentiation among many theoretically plausible mechanistic alternatives.

The study of kinetic isotope effects is also useful in establishing the magnitude of errors involved in tracer experiments and in providing experimental verification of theoretical calculations regarding the nature of the transition states in various types of bond-breaking processes.

The above applications as well as the general methods for evaluating kinetic isotope effects have been elegantly discussed and reviewed by Raaen and his co-authors.<sup>2</sup>

However, kinetic isotope effects in chemical reactions are frequently difficult to measure because of the problems involved in obtaining sufficiently re-

producible direct kinetic data on individual isotopic species. This difficulty is particularly evident in heterogeneous reaction systems, where it may prove impossible to maintain even an approximate control over all the significant reaction variables.

Frustration over attempts to obtain such direct kinetic data for the oxidation of alcohols by silver carbonate on Celite,<sup>3</sup> a combination known as Fetizon's reagent,<sup>4</sup> led us to utilize a double isotopic labeling technique which permits different isotopic species to be studied in a single reaction mixture and the determination of the kinetic isotope effect without a concurrent determination of the kinetics of the reaction.

It must be emphasized that theoretical treatments relating kinetic isotope effects to the isotopic composition of reactants and products have been previously described.<sup>5</sup> Also the use of one isotope as a

(1) C. J. Collins and N. S. Bowman, "Isotope Effects in Chemical Reactions," ACS Monograph 167, Van Nostrand-Reinhold, Princeton, N. J., 1970.

(2) V. F. Raaen, G. A. Ropp, and H. R. Raaen, "Carbon 14," McGraw-Hill, New York, N. Y., 1968, pp 47–83.

(3) F. J. Kakis, "On the Mechanism of the Oxidation of Alcohols by Silver Carbonate," 7th Western Regional Meeting of the American Chemical Society, Anaheim, Calif., Oct 1971.

(4) M. Fetizon and M. Gouffier, *C. R. Acad. Sci., Ser. C*, **276**, 900 (1968).

(5) J. Ying-Peh Tong and P. E. Yankwich, *J. Phys. Chem.*, **61**, 540 (1957).

tracer for another is well known.<sup>6-7</sup> Thus no originality in this respect is either claimed or intended.

We have utilized these concepts, integrated them into a single, coherent, and generally applicable procedure, critically examined its strengths and limitations, and shown experimentally that it can yield reproducible kinetic isotope data in a system where direct kinetic measurements were found to be difficult to obtain.

**Theory.**—Consider a mixture of two isotopically distinct reactants A and B, and assume A additionally to be labeled in a manner not affecting its kinetic properties in the reaction to be studied. Let the reaction mixture originally contain mole fractions  $x_a$  and  $x_b$  of A and B, respectively, and let  $Q_0$  be the initial specific radioactivity (per mole) of pure A. After the reaction has been allowed to proceed for an unknown amount and for an arbitrary time interval, let the unreacted reactant mixture then have molar specific activity  $Q_r$  and the mixture of products  $Q_p$ . The above-described information suffices to determine the ratio of the reaction rate constants for A and B.

The analysis is based on the assumption that the numbers of moles of A and B,  $n_a$  and  $n_b$ , respectively, are governed by rate equations of the general forms

$$\frac{-dn_a}{dt} = k_a n_a f(n_a + n_b) \quad (1a)$$

$$\frac{-dn_b}{dt} = k_b n_b f(n_a + n_b) \quad (1b)$$

where  $k_a$  and  $k_b$  are the rate constants for reaction of isotopic species A and B, and  $f(n_a + n_b)$  is a function containing the remainder of the expression for the rate. This function may depend upon time, upon the concentrations of other species (and therefore upon the extent of reaction and ultimately upon  $n_a + n_b$ ), and upon various other factors, but it is specifically assumed that the same function occurs in the rates for both isotopic species. It is further assumed that the difference in rate among isotopically substituted reactants is first order in the reactant concentration, although the overall rate may be of higher order. This assumption avoids the necessity for considering processes in which several isotopic molecules are involved in rate-determining reaction steps.

Combining eq 1a and 1b, we may find

$$\frac{dn_a}{k_a n_a} = \frac{dn_b}{k_b n_b} \quad (2)$$

and therefore, at any time,

$$\frac{n_a}{n_a^0} = \left(\frac{n_b}{n_b^0}\right)^K \quad (3)$$

where  $K = k_a/k_b$  and  $n_a^0$  and  $n_b^0$  are the initial numbers of moles of A and B. The rate-constant ratio  $K$  characterizes the isotope effect.

We now wish to relate the activity data to the isotope effect. Using the fact that the specific activity of pure A is  $Q_0$ , we see that the reactant activity value  $Q_r$  implies that the mole fraction of A in the unreacted sample is  $Q_r/Q_0$ , so

$$\frac{n_a}{n_a + n_b} = \frac{Q_r}{Q_0} \quad (4)$$

Similarly, noting that  $n_a^0 - n_a$  and  $n_b^0 - n_b$  are the numbers of moles of A and B converted to products, that activity value  $Q_p$  yields

$$\frac{n_a^0 - n_a}{(n_a^0 - n_a) + (n_b^0 - n_b)} = \frac{Q_p}{Q_0} \quad (5)$$

Equations 4 and 5 may now be combined with eq 3 and solved for  $K$ , giving

$$K = 1 + \frac{\log \left[ \frac{x_b Q_r}{x_a (Q_0 - Q_r)} \right]}{\log \left[ \frac{(Q_0 - Q_r)}{(Q_p - Q_r)} \left( \frac{Q_p - x_a Q_0}{x_b Q_0} \right) \right]} \quad (6)$$

**Scope and Limitations.**—While eq 6 is valid over the entire course of an isotopically mixed reaction, it should be pointed out that the last term on its right-hand side approaches an indeterminate form of the type 0/0 if  $Q_p$  and  $Q_r$  are determined in the very first stages of a reaction or if the isotope effect is very small. In both these cases the experimental data can still provide a good determination of the isotope effect but precision will be required in carrying out the numerical evaluation. Also it may be necessary to introduce corrections to compensate for the apparent lagging of the heavy isotope.<sup>8</sup> If a reaction proceeds so slowly that it is practical to study the initial rate, eq 6 reduces to the simple form

$$K = \frac{x_b}{x_a} \left( \frac{Q_p}{Q_0 - Q_p} \right) \quad (7)$$

If, on the other hand,  $Q_p$  and  $Q_r$  are determined very late in the course of a reaction, the last term of eq 6 approaches an indeterminate form of the type  $\infty/\infty$ , with physical significance that as the reaction moves toward completion we lose all information about the isotope effect except its direction.

An examination of the foregoing equations suggests that the most precise results will be obtained when the activities of unreacted material,  $Q_r$ , and product,  $Q_p$ , differ as much as possible. This situation can be best achieved by having the more rapidly reacting isotopic species initially present in small concentration, and making assays as early as practical in the reaction course.

The described technique is applicable when the reactant under study is available as an isotopic mixture of known composition, and when one of the isotopic species has an additional labeling lacking in the other.

The second label must be sufficiently removed from the reactive site so that it is in no way involved in the rate-determining process. Its presence is merely a convenient means for monitoring the reaction. Although in our experiments we have used a radioactive element as the second label, this is not a limitation of the method. Any isotope can be used as a tracer, the choice being limited only by the available means for establishing the isotopic composition of the reaction mixtures.

If the object is to measure highly precise or very small kinetic isotope effects and traditional direct kinetic measurements are possible, then obviously this will not be the method of choice. However,

(6) V. F. Raean, T. K. Dunham, D. D. Thompson, and C. J. Collins, *J. Amer. Chem. Soc.*, **85**, 3497 (1963).

(7) D. E. Schmidt, Jr., W. G. Nigh, C. Tanzer, and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 5849 (1969).

(8) For an extensive discussion of C. J. Collins and M. H. Lietzke, *J. Amer. Chem. Soc.*, **81**, 5379 (1959).

in some instances this may be the only way to obtain information about kinetic isotope effects.

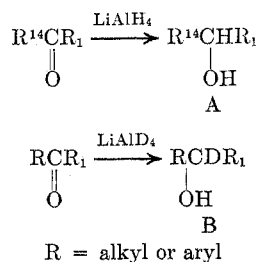
Thus, we consider the above method as particularly advantageous when reproducible conditions cannot be maintained for different reacting samples, when the significant factors governing the reaction are uncontrollably varying with time, and even when the act of removing an aliquot sample for analysis causes an unknown disturbance in the reacting system.

The double labeling also permits analysis to be based on sampling of the reaction system and avoids the necessity of quantitative isolation of the various components in the reaction mixtures. Finally this method can be used as an independent check of kinetic isotope effect data obtained by the conventional methods.

### Application, Results, and Discussion

The oxidation of alcohols by silver carbonate precipitated on Celite<sup>4</sup> is a heterogeneous reaction which takes place under neutral conditions and involves the simple reflux of the oxidizing agent with a solution of the alcohol. For the past 2 years we have been investigating the mechanism of this reaction.<sup>3</sup> During the course of this investigation we have decided to measure the primary and secondary deuterium isotope effect; however, we discovered that it was very difficult to obtain reproducible data from straightforward kinetic determinations. In the first place the reaction showed induction periods of varying times. Furthermore, considerable variation in the extent of oxidation was at times observed even on identically prepared samples maintained at the same constant temperature for the same amount of time. These discrepancies can arise from a variety of factors which are difficult to control, such as the mesh distribution or state of aggregation of the solid oxidizing agent, the rate of stirring and reflux, etc. In view of this, it became apparent that the only valid comparison of the rate of oxidation of the protium and deuterium-labeled alcohols would be one involving the simultaneous oxidation of a mixture of the two in the same vessel. Only in this way can one be assured that the conditions were identical. To this end mixtures of nonradioactive deuterated alcohols and radioactive (C-14 labeled) protium alcohols of known specific activity were simultaneously oxidized.

The choice of the particular substrates used was dictated by their availability. Some of the immediate precursor ketones of the alcohols used were on hand from a previous study.<sup>9</sup> Other samples were privately supplied.<sup>10</sup> In each case the ketones were first reduced to the corresponding alcohols by either lithium hydride or lithium aluminum deuteride as follows.



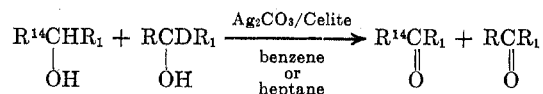
(9) F. J. Kakis, D. Brase, and A. Oshima, *J. Org. Chem.*, **36**, 4117 (1971).

(10) We are indebted to Dr. C. J. Rossi for supplying us with some of the radioactive samples and for performing some of the assays.

After suitable purification alcohol A was assayed for <sup>14</sup>C and its specific activity  $Q_0$  was determined. Alcohol B was examined by nmr to ensure that it had been completely deuterated. Subsequently a mixture of A and B was prepared and homogenized by dissolving both in a suitable solvent, which was then evaporated to recover the crystals. The crystals were then dried and the mixture was assayed for radioactivity. From the known specific activity  $Q_0$  of pure A and that of the mixture  $Q_m$  the mole fractions  $x_a$  and  $x_b$  were calculated as follows.

$$x_a = \frac{Q_m}{Q_0} \text{ and } x_b = 1 - x_a$$

The mixtures of A and B were then partially oxidized.



At the end of the oxidation the reaction mixtures contained ketonic products and unreacted alcohols. These were separated by thin layer chromatography and purified. The specific activities of the pure unreacted starting material  $Q_r$  and of the pure product  $Q_p$  were then determined by <sup>14</sup>C assays. Substitution of all this data into eq 6 permitted the calculation of the kinetic isotope effect.<sup>11</sup>

Thirteen different alcohols were tested by this method. Each oxidation was performed in triplicate, the reported values being the average of these determinations.

The experimental data and the calculated results are summarized in Table I. Retaining only two significant figures, we find an average value for  $K$  of  $3.0 \pm 0.1$ . The only other information on the deuterium isotope effect in the silver carbonate oxidation of alcohols comes from the work of Eckert, *et al.*,<sup>12</sup> who studied the oxidation of norbornanols by gas chromatography. They report an isotope effect between 3 and 4. Thus we conclude that the described technique can afford reliable kinetic isotope effect data within the limitations discussed.

### Experimental Section

**General.**—Melting points were taken on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Nmr spectra were recorded on a Varian A-60A or T-60 spectrometer, with tetramethylsilane as an internal standard. Infrared spectral data were recorded on a Beckman IR-5A spectrophotometer. Radioactivity levels of the various carbon-14 labeled compounds were determined by dry combustion of the samples to carbon dioxide, which was collected in an ionization chamber and assayed in the usual way<sup>13</sup> using a Cary Model 31 vibrating-reed electrometer. All the deuterated alcohols were obtained from the corresponding ketones by lithium aluminum deuteride reduction. The procedure used in each case was identical with that described below for the synthesis of deuterated 1,2,2-triphenylethanol. All of the carbon-14 labeled protium alcohols were similarly obtained from their carbon-14 labeled ketone precursors<sup>9,10</sup> by lithium aluminum hydride reduction. The silver carbonate oxidations of the various samples followed a procedure exactly analogous to that described below for the oxidation of 1,2,2-triphenylethanol.

(11) To facilitate the computations a simple program was written in basic Fortran.  $K$  was then calculated with the aid of a National Cash Register CENTURY 100 computer. This program is available from the author upon request.

(12) M. Eckert-Maksic, Lj. Tusek, and D. E. Sunko, *Croat. Chim. Acta*, **43**, 79 (1971).

(13) V. F. Raess and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

TABLE I  
 ALCOHOLS OXIDIZED, RADIOACTIVITY DATA, AND CALCULATED RESULTS

| Compd <sup>a</sup>                                   | $x_a$  | $x_b$  | $Q_0$ ,<br>mCi/mol <sup>b</sup> | $Q_r$ ,<br>mCi/mol <sup>b</sup> | $Q_p$ ,<br>mCi/mol <sup>b</sup> | $K$<br>( $K_H/K_D$ ) |
|------------------------------------------------------|--------|--------|---------------------------------|---------------------------------|---------------------------------|----------------------|
| 1,2,2-Triphenylethanol <sup>c</sup>                  | 0.5056 | 0.4944 | 4.755                           | 1.623                           | 3.304                           | 3.0                  |
| 1,2,2-Tri- <i>p</i> -anisylethanol <sup>c</sup>      | 0.3279 | 0.6721 | 8.013                           | 1.832                           | 4.393                           | 3.1                  |
| 1,2,2-Tri- <i>p</i> -tolylethanol <sup>c</sup>       | 0.4358 | 0.5642 | 7.837                           | 2.176                           | 4.927                           | 3.0                  |
| 1,2-Diphenylethanol <sup>d</sup>                     | 0.2795 | 0.7205 | 8.276                           | 1.791                           | 4.077                           | 2.9                  |
| 1,3-Diphenyl-2-propanol <sup>c</sup>                 | 0.4478 | 0.5522 | 6.055                           | 2.367                           | 4.188                           | 3.1                  |
| Benzhydrol <sup>d</sup>                              | 0.3569 | 0.6431 | 7.537                           | 2.018                           | 4.296                           | 2.9                  |
| Di- <i>o</i> -tolylmethanol <sup>d</sup>             | 0.3027 | 0.6973 | 8.210                           | 1.952                           | 4.461                           | 3.2                  |
| Di- <i>p</i> -tolylmethanol <sup>d</sup>             | 0.2868 | 0.7132 | 7.976                           | 1.897                           | 4.231                           | 3.2                  |
| 1-Phenyldodecanol <sup>d</sup>                       | 0.4680 | 0.5320 | 5.932                           | 2.296                           | 4.056                           | 2.9                  |
| Phenyl- <i>p</i> -tolylcarbinol <sup>d</sup>         | 0.3645 | 0.6355 | 7.562                           | 1.997                           | 4.506                           | 3.2                  |
| 1,3-Diphenyl-1-propanol <sup>d</sup>                 | 0.4063 | 0.5937 | 8.105                           | 1.699                           | 4.689                           | 3.0                  |
| 1,2-Diphenyl-1-decanol <sup>d</sup>                  | 0.4271 | 0.5729 | 4.972                           | 1.832                           | 3.259                           | 2.9                  |
| 1-Phenyl-2,2-di- <i>p</i> -tolylethanol <sup>d</sup> | 0.3723 | 0.6277 | 6.979                           | 1.974                           | 4.267                           | 3.2                  |

<sup>a</sup> Registry numbers for deuterated (<sup>14</sup>C) form: 39994-06-4 (39994-07-5), 39994-08-6 (39994-09-7), 39994-10-0 (39994-11-1), 39994-12-2 (39994-13-3), 39994-14-4 (39994-15-5), 17498-07-6 (39994-17-7), 39994-18-8 (39994-19-9), 39994-20-2 (39994-21-3), 39994-22-4 (39994-23-5), 39994-24-6 (39994-25-7), 39994-26-8 (39994-27-9), 39994-28-0 (39994-29-1), 39994-30-4 (39994-31-5). <sup>b</sup> The values shown are the average of three assays. The maximum deviation observed in these measurements was less than 1%. <sup>c</sup> Labeled on the  $\beta$  carbon. <sup>d</sup> Ring labeled.

**Deuterated 1,2,2-Triphenylethanol [Ph<sub>2</sub>CHC(OH)DPh] (B).**—A magnetically stirred suspension of excess lithium aluminum deuteride (3 g) in anhydrous ether (200 ml) was treated gradually with a solution of analytically pure (mp 139–140°) phenylbenzhydryl ketone (2.72 g, 0.01 mol) in anhydrous ether. Solution of the ketone in the ether was achieved by equipping the flask with a Soxhlet extractor and placing the ketone crystals in an extraction thimble.

The mixture was continually stirred and refluxed gently with a hot water bath over a period of 4 hr, after which it was cooled in a Dry Ice-isopropyl alcohol bath. The decomposition of the complex and the destruction of the excess hydride was accomplished by the cautious successive addition of water (3 ml), 15% sodium hydroxide solution (3 ml), and again water (9 ml). This procedure gave a white, crystalline precipitate of inorganic salts which was filtered in a canted glass filter funnel and washed with ether. The organic phase was dried over anhydrous magnesium and sodium sulfates. On evaporation of the solvents, a viscous oil was obtained which was crystallized by triturating with a few milliliters of hot hexane. After two recrystallizations from hexane a pure sample (mp 81–82°) of deuterated 1,2,2-triphenylethanol was obtained. The yield was quantitative. The identity and isotopic purity of the product were confirmed by infrared and nmr spectroscopy.

**Carbon-14 Labeled 1,2,2-Triphenylethanol [Ph<sub>2</sub><sup>14</sup>CHC(OH)HPh] (A).**—This compound was prepared from carbon-14 labeled phenylbenzhydryl ketone<sup>9</sup> by lithium aluminum hydride reduction. The procedure used was identical with the one described above.

**Partial Oxidation of a Mixture of Ph<sub>2</sub><sup>14</sup>CHC(OH)HPh (A) and Ph<sub>2</sub>CHC(OH)DPh (B).**—A sample (0.99500 g) of radioactive (4.755 mCi/mol) protium alcohol A was mixed with a sample (0.99495 g) of the deuterated alcohol B. The mixture was then dissolved in spectral grade chloroform to homogenize the samples.

The chloroform was subsequently removed by rotatory evaporation and the crystals were dried under vacuum over phosphorus pentoxide. The mixture was then assayed for carbon-14 and found to have a specific activity of 2.404 mCi/mol. From this data the exact mole fractions of A ( $x_a = 0.5056$ ) and B ( $x_b = 0.4944$ ) were calculated.

A portion of this mixture (552.5 mg, ca. 0.002 mol) was added to a suspension of predried silver carbonate–Celite reagent<sup>4</sup> (638 mg, ca. 0.0011 mol) in anhydrous benzene (50 ml). After refluxing for several hours the reaction was stopped, the solids were filtered off, and the benzene was evaporated. The residue consisting of unreacted alcohols and phenylbenzhydryl ketone was chromatographed on thin layer plates coated with fluorescent silica and eluted with benzene. This afforded a good separation of the alcohols from the ketone. The individual samples were then isolated and purified, the alcohols by successive recrystallizations from hexane and the ketone by sublimation followed by recrystallization from methanol. The pure samples were then assayed for carbon-14 and the specific activities of the unreacted alcohols ( $Q_r = 1.623$  mCi/mol) and of the products ( $Q_p = 3.304$  mCi/mol) were determined. When all of the above data were substituted into eq 6, the calculated value for  $K$  was 3.0114. Repetitive oxidations of the same mixture gave similar results.

**Registry No.**—Ag<sub>2</sub>CO<sub>3</sub>, 534-16-7.

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