amount of polymer obtained in the various experiments is shown in Table IV.

Decomposition of Polymeric Thiobenzaldehyde.—A weighed amount (0.3 g.) of polymeric thiobenzaldehyde was dissolved in 25 ml. of bromobenzene and the solution deaerated with nitrogen at room temperature. It was then refluxed for 16 hr. under a nitrogen atmosphere. It was observed that the solution became blue soon after heat was applied. The blue color reached a maximum during the first hour of reflux and then faded rapidly, the solution finally becoming light brown. Infrared analysis of the products showed stilbene had been formed in 31% yield. Some trithiobenzaldehyde (0.07 g.) was also isolated. The other products were not identified.

In a second experiment using half as concentrated a solution of the polymeric thioaldehyde the stilbene yield was higher (40%).

Purification of Solvents. Bromobenzene and Chlorobenzene.—The highest grade commercial products were carefully fractionally distilled; bromobenzene, b.p. 155–156°; chlorobenzene, b.p. 131–132°. **1-Chloronaphthalene** (Eastman Kodak Co. white label) was washed with dilute sodium bicarbonate, dried over sodium sulfate, and fractionally distilled under reduced pressure, b.p. 152–153° (40 mm.).

The best grade commercial **2-methylnaphthalene** was fractionally crystallized four times, about half of the original material being discarded in the process. The remaining hydrocarbon was then fractionally distilled, b.p. 129–130° (25 mm.). **Benzonitrile** was steam distilled; the distillate was extracted with ether; the ether solution was washed with dilute sodium carbonate, dried overnight with calcium chloride, and the ether removed. The residue was fractionally distilled, b.p. 96° (40 mm.). **Methyl benzoate** (Eastman Kodak Co. white label) was washed with dilute sodium bicarbonate, then with water, dried over sodium sulfate and finally fractionally distilled under reduced pressure, b.p. 104–105° (39 mm.). **Nitrobenzene** (Eastman Kodak Co. white label) was fractionally distilled under reduced pressure, b.p. 115° (40 mm.). It gave no measurable acidity when tested in the fashion described by Rosin.[28]

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(28) J. Rosin, "Reagent Chemicals and Standards," 1st. ed., D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 285.

COLUMBIA, S. C.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY[1]]

Studies Involving Isotopically Labeled Formic Acid and its Derivatives.[1,2] V. Studies of the Decarbonylation of Formic, Benzoylformic and Triphenylacetic Acids in Sulfuric Acid

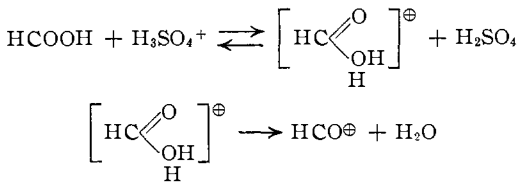
BY GUS A. ROPP

RECEIVED MAY 20, 1959

By employing deuterium and carbon-14 isotope fractionation studies, carbon-14 tracer studies and oxygen-18 isotope exchange studies, definite information has been obtained about the mechanism of decarbonylation of formic acid, triphenylacetic acid and benzoylformic acid in concentrated sulfuric acid. The experimental results are in accord with previously proposed mechanisms of decarbonylation of formic and benzoylformic acids. In the case of the triphenylacetic acid decarbonylation, strong evidence is presented that a previously proposed mechanism is incorrect. A tentative mechanism for the decarbonylation of triphenylacetic acid which will account for the experimental observations has been suggested. An oxygen-18 exchange between carbon monoxide and concentrated sulfuric acid has been observed. A general discussion of isotopic methods which are applicable to the study of decarbonylation reactions and other similar reactions is included. Specific activity–per cent reaction curves that facilitate rapid computation of kinetic isotope effects are presented.

I. Introduction

The decarbonylation, or loss of carbon monoxide, by carboxylic acids in concentrated sulfuric acid occurs only with acids in which the group attached to the carboxyl group is one of a very few specific types. The principal acids which decarbonylate are formic,[3] oxalic[4] and triphenylacetic[5] acids, α-hydroxy acids,[6] α-keto acids[7] and acids in which a tertiary alkyl group is attached to the carboxyl group. In many instances the decarbonylation has been reported to proceed quantitatively. Little is known about the details of the mechanisms of any of these reactions. The relationship between log k, the logarithm of the pseudo-first-order rate constant, and the acidity function[7a,8] of the sulfuric acid used has been studied for several decarbonylations. In some instances the activation energies have been measured; in others the effects of various added chemicals on the specific reaction rates have been investigated. The usual view taken of the mechanism of these reactions is that they proceed in a manner similar to that proposed by Hammett[3c] for the decarbonylation of formic acid in excess concentrated sulfuric acid



$$HCOOH + H_3SO_4^+ \rightleftharpoons \left[HC\begin{matrix} \nearrow O \\ \searrow \underset{H}{OH} \end{matrix}\right]^{\oplus} + H_2SO_4$$

$$\left[HC\begin{matrix} \nearrow O \\ \searrow \underset{H}{OH} \end{matrix}\right]^{\oplus} \longrightarrow HCO^{\oplus} + H_2O$$

$$HCO^{\oplus} + H_2SO_4 \longrightarrow CO + H_3SO_4^{\oplus}$$

Hammett does not explain which is the rate-determining step except to state that if either the first or second steps determined the rate, the observed relation between the rate constant and the acidity function of the sulfuric acid should follow. Hammett also states, "whatever the detailed mechanism (of acid-catalyzed decarbonylation reactions) they necessarily involve the separation of the group attached to the carboxyl group in the form of a positive ion." Presumably,

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(1) Operated by Union Carbide Corp. for the U. S. Atomic Energy Commission.

(2) Preceding paper, C. E. Melton and Gus A. Ropp, THIS JOURNAL, **80**, 5573 (1958).

(3) (a) E. Schierz, THIS JOURNAL, **45**, 447 (1923); (b) R. De Rigbt, *ibid.*, **55**, 4761 (1933); (c) L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 283.

(4) D. Lichty, *J. Phys. Chem.*, **11**, 224 (1907).

(5) H. Dittmar, *J. Chem. Phys.*, **33**, 533 (1929).

(6) (a) E. Whitford, THIS JOURNAL, **47**, 953 (1925); (b) H. Dittmar, *ibid.*, **52**, 2746 (1930); (c) E. Wiig, *ibid.*, **52**, 4729 (1930).

(7) (a) W. W. Elliott and D. L. Hammick, *J. Chem. Soc.*, 3402 (1951); (b) K. Banholzer and H. Schmid, *Helv. Chim. Acta*, **39**, 548 (1956).

(8) L. P. Hammett, *Chem. Revs.*, **16**, 67 (1935).

therefore, a carboxylic acid might be expected to decarbonylate only if the positive ion fragment left after separation of the carboxyl group is either stable in sulfuric acid or can readily react in sulfuric acid to yield another stable ion. Of the carboxylic acids known to decarbonylate readily in sulfuric acid, almost all have structures which fit in with the general idea of the separation of a stable or stabilizable positive ion from the carboxyl group. Thus formic acid would yield a proton and triphenylacetic acid, the triphenylmethyl carbonium ion, which should be stabilized by resonance. Oxalic acid and α-hydroxy acids, according to this simple picture, should yield, respectively, the ions $COOH^{\oplus}$ and $R_2C^{\oplus}\text{-}OH$ which should stabilize themselves by immediate loss of a proton to the sulfuric acid. In the cases of α-keto acids and acids of the type $R_3C\text{-}COOH$, the charges on the groups $R\text{-}\overset{\oplus}{C}O$ and $R_3C^{\oplus}$ would presumably be sufficiently stabilized by resonance or inductive effects to permit decarbonylation to occur.

As both Hammett and Hine[9] have pointed out, however, there are certainly differences in some of the mechanistic details among sulfuric acid-catalyzed decarbonylations since the reactions are variously affected by changes in H_0, the acidity function of the sulfuric acid. Elliott and Hammick[7a] have recounted some of the variations in the acidity function–log k relationships among the various decarbonylation reactions; thus log k *vs.* H_0 plots have slopes very near unity for decarbonylation of formic acid and malic acid and for decarbonylation of oxalic acid in 90 to 96% sulfuric acid. This has been taken to indicate that each of these reactions proceeds *via* a monoacidium ion, *i.e.*, *via* an intermediate formed by attachment of a single proton to the carboxyl group. As a slope of very nearly 2 was found for decarbonylation of citric and benzoylformic acids and for decarbonylation of oxalic acid in 98 to 100% sulfuric acid, each of these reactions is thought to proceed *via* a diacidium ion, *i.e.*, *via* an intermediate formed by attachment of two protons to the organic molecule. The decarbonylation of triphenylacetic acid in 93 to 97% sulfuric appears to be exceptional in that the slope is between 2 and 3. Recently Deno and Taft[10] have correlated the data of Dittmar[5] for decarbonylation of triphenylacetic acid using J_0, an acidity function which takes into account the activity of the 4 to 7% water in the sulfuric acid. They conclude that their results remove the necessity of attempting to interpret the nonintegral slope[7a] in the plot of log k *vs.* H_0 and propose a mechanism involving an equilibrium concentration of an oxocarbonium ion and cleavage of the carbon–carbon bond to the α-carbon atom as the rate-determining step

$$(C_6H_5)_3CCOOH + H^{\oplus} \rightleftarrows H_2O + (C_6H_5)_3C\text{-}CO^{\oplus}$$

$$(C_6H_5)_3C\text{-}CO^{\oplus} \xrightarrow[\text{step}]{\text{slow}} (C_6H_5)_3C^{\oplus} + CO\uparrow$$

$$(C_6H_5)_3C^{\oplus} + H_2O \xrightarrow[\text{reaction}]{\text{quenching}} (C_6H_5)_3COH + H^{\oplus}$$

More recently, Banholzer and Schmid[7b] have discussed the mechanism of the decarbonylation of benzoylformic acid. Their experimental work, however, proved only that the carbon monoxide released from benzoylformic acid in concentrated sulfuric acid arises from the carboxyl group, and hence gave little information about the details of the decarbonylation mechanism. With a few exceptions, most of the attempts to study the mechanisms of decarbonylation of carboxylic acids in concentrated sulfuric acid have centered around determining rate-acidity function relationships. Since such studies of the form of the observed acid catalysis are something less than perfect means of studying a reaction mechanism, it is highly desirable that decarbonylation reaction mechanisms should be investigated by whatever other tools are available.

Among the other tools which can be employed effectively are isotopic labeling. The use of isotopic exchange[11,12] studies and the study of rate processes through evaluation of kinetic isotope effects[12] are now widely accepted means of investigating reaction mechanisms. Isotope rate effects due to substitution of carbon-14 and carbon-13 as well as those due to substitution of deuterium and tritium can now be evaluated accurately[13] and can often be employed as criteria[13] of reaction mechanisms.

II. Isotopic Studies

A. Isotopic Methods Which Are Applicable to the Study of Decarbonylation Reactions and Related Reactions. (1) Test for Reversibility of a Reaction.—A simple test for reversibility is to mix an isotopically-labeled product with unlabeled reactant or reactants under specified conditions. Usually, a reactant which would become labeled if the reaction were reversible, is isolated, carefully purified, and isotopically assayed. If the purified sample is found to be isotopically labeled, reversibility of the reaction is indicated.

(2) Simple Tracing of a Labeled Carbon Atom during a Reaction.—In some cases a product might be formed from either of two or more unequivalent carbon atoms of a reactant. In such cases the decision as to which carbon atom or atoms in the reactant supply the carbon to form the product can usually be made with the help of isotopic labeling. If the product is isotopically labeled only when the reactant is labeled in one particular position, the carbon in the product must arise from the carbon in that position.

(3) Isotope Fractionation Studies of Rate Processes.—The determination of the rate isotope effect, for example k_{12}/k_{14} in the case of fractionation due to substitution of carbon-14 for carbon-12, is frequently definitive in identifying a rate-limiting process in a reaction scheme. The rate isotope

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[9] Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 291, 292.

[10] N. C. Deno and R. W. Taft, Jr., This Journal, **76**, 248 (1954).

[11] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951.

[12] S. L. Friess and A. Weissberger, "Investigation of Rates and Mechanisms of Reactions," Vol. VIII of "Techniques of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, pp. 69–99 and 316.

[13] E. Grovenstein, Jr., and Gus A. Ropp, This Journal, **78**, 2560 (1956); footnote 8 of that paper discusses the relative advantages of using carbon-14 and carbon-13 in isotope fractionation studies of reaction mechanisms.

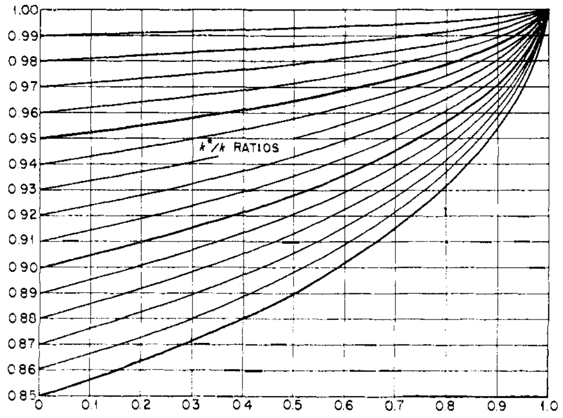

Fig. 1.

effect has also been used to estimate the nature of the bonds in the activated complex[14] of a rate process. For convenience rate isotope effects have been classified as *primary* or *secondary*, a *primary* isotope effect being one in which a bond or bonds to the labeled atom are broken[15] in the rate-limiting process, and a *secondary* effect being one in which a bond or bonds to the labeled atom are relatively little affected during the rate-limiting step. This classification is admittedly arbitrary and could not be defended rigorously. It is nevertheless very helpful in discussions of isotope fractionation. Generally speaking, *secondary* isotope effects are smaller than *primary* effects, that is to say, the ratio of the rate constants of the isotopically labeled molecules in the case of *secondary* effects differs less from unity than it does in the case of *primary* effects.

Intermolecular carbon-14 kinetic isotope effect ratios, that is k_{12}/k_{14} or k_{14}/k_{12}, are usually evaluated experimentally by one of three methods which will be listed here as (a), (b) and (c). Various researchers have, of course, altered these methods somewhat to suit their own needs, but the ideas upon which all these methods are based are those summarized here. The same general methods have also been used to evaluate carbon-13, nitrogen-15, oxygen-18, and other kinetic isotope effect ratios. The methods are as follows:

(a) *The molar specific activity of the accumulated reaction product up to a measured percentage reaction—preferably a small percentage reaction—is compared with the molar specific activity of the starting material*[16] *or with the molar specific activity of the product accumulated at 100% reaction.* A simple relationship exists[16a] between the ratio of the isotopic rate constants, k^*/k, the fraction of reaction, f, and r, the ratio of the molar specific activity of the product of partial reaction to the molar specific activity of the starting material

$$k^*/k = \log(1 - rf)/\log(1 - f)$$

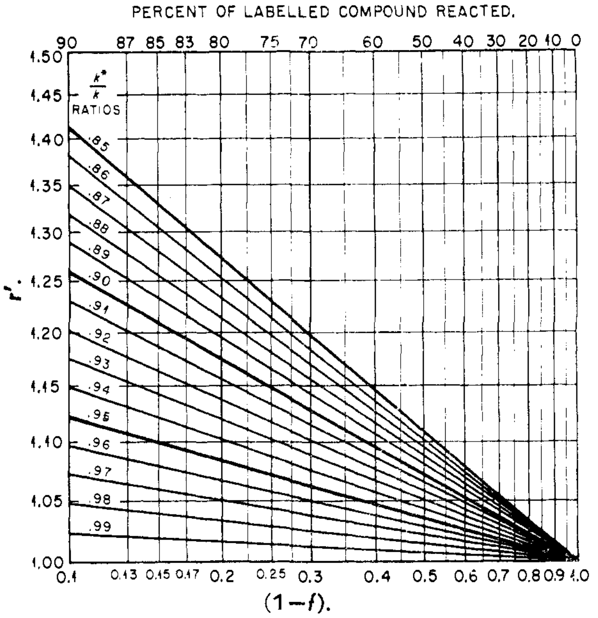

Fig. 2.

Figure 1 shows graphically the values of r at different values of f for the k^*/k ratios of 0.85 to 1.00 which are listed on the ordinates axis. At values of f approaching 0, r becomes essentially equal to k^*/k. If f is unity r is unity for any value of k^*/k. This is necessarily true for an *intermolecular* isotope effect though not for an *intramolecular* isotope effect. Use of Fig. 1 is convenient for the rapid estimation of k^*/k ratio from isotopic data. Experimentally measured values of r and f determine a point on the graph through which a curve is drawn, the direction being guided by interpolation between the nearest printed curved lines. The k^*/k ratio sought is given by the intersection of the drawn curve with the ordinates axis.

(b) *The molar specific activity of reactant remaining after a measured percentage reaction—preferably a high percentage reaction—is compared with the molar specific activity of the starting material or with the molar specific activity of product accumulated at 100% reaction.* Beginning with the Stevens and Attree[16a] equation, the relationship between the ratio of the isotopic rate constants, k^*/k, the fraction of reaction, f, and the ratio, r', of the molar specific activity of residual reactant to the molar specific activity of the starting material can be shown to be

$$k^*/k = [\log r'/\log(1 - f)] + 1$$

For convenience in rapid estimation of values of k^*/k from isotopic data by this method, two graphs showing the relationship between r' and f or $(1 - f)$ for fifteen values of k^*/k are given. Figure 2 covers the range 0 to 90% reaction. Figure 3 covers the range 90 to 99% reaction. In practice, experimentally determined values of r' and $(1 - f)$ locate a point on one of the two graphs. The corresponding k^*/k ratio is estimated by interpolation between the nearest diagonal lines. From Figs. 2 and 3 it is apparent that successful use of this method requires that the percentage

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(14) H. S. Johnston, W. A. Bonner and D. J. Wilson, *J. Chem. Phys.*, **26**, 1002 (1957).

(15) The question as to whether rate isotope fractionation occurs in bond-making processes has not been completely settled.

(16) (a) W. H. Stevens and R. Attree, *Can. J. Res.*, **B27**, 807 (1949); (b) J. Bigeleisen, *Science*, **110**, 14 (1949); (c) G. A. Ropp, *Nucleonics*, **10**, 22 (1952).

reaction be measured carefully. Furthermore, this method is usually applied by carrying the percentage reaction to 50% or preferably much higher; consequently, the reaction being studied must be essentially free of side reactions.[17]

(c) *The molar specific activity of a small increment of product formed at a specific time during a reaction—that is at a known value of f—is compared with the molar specific activity of the starting material or with the molar specific activity of the product accumulated at 100% reaction.* This method has found few applications so far because it is usually impractical to collect a small product increment at a known percentage reaction. However, it can be useful in studies of some reactions in which the product is evolved as a gas, is separated as a precipitate or can be continuously extracted by some means as rapidly as it forms. This method of studying kinetic isotope effects has been discussed by Downes.[17a] A relationship between k^*/k, f and r'', the ratio of the molar specific activity of the product increment to the molar specific activity of the starting material, can be most directly derived as follows: (i) At any time, t, the increment of product formed (moles) in the time interval, dt, for a first-order reaction is

$$\mathrm{d}n = kN_0e^{-kt}\,\mathrm{d}t$$

where k is the first-order rate constant and N_0 is the number of moles of reactant at time $t = 0$.

(j) For competitive isotopic reactions in the same batch, the ratio of two such expressions gives

$$\frac{\mathrm{d}n^*}{\mathrm{d}n} = \frac{k^*N_0{}^*e^{-k^*t}\,\mathrm{d}t}{kN_0e^{-kt}\,\mathrm{d}t}$$

The time differentials cancel. For small increments of product the differentials are replaceable by integral quantities, giving

$$\frac{n^*}{n} = \frac{k^*N_0{}^*e^{-k^*t}}{kN_0e^{-kt}}$$

or

$$\frac{n^*}{n} = \frac{k^*}{k} \times \frac{N_0{}^*}{N_0} \times e^{k\left(1 - \frac{k^*}{k}\right)t}$$

(k) For the unlabeled molecules, if the number of moles of reactant remaining at time t is N, then

$$N/N_0 = e^{-kt}$$

(l) Dividing the final equation from (j) by equation (k) after conversion to logarithmic form gives

$$\frac{\ln\left[\frac{n^*}{n}\Big/\frac{k^*}{k} \times \frac{N_0{}^*}{N_0}\right] = k\left(1 - \frac{k^*}{k}\right)t}{\ln[\mathrm{N}/\mathrm{N}_0] \qquad\qquad = -kt}$$

which reduces to

$$\log\left[\frac{n^*}{n}\Big/\frac{N_0{}^*}{N_0}\right] - \log\left[\frac{k^*}{k}\right] = \left[\frac{k^*}{k} - 1\right]\log\,[N/N_0]$$

(m) $N/N_0 = (1 - f)$, where f is the fraction of the reaction completed at the time the product increment is collected.

(n) Now n^*/n is proportional to the molar specific activity of the product increment and $N_0{}^*/N_0$ is proportional to the molar specific activity of the starting material. Therefore, substitute r'', the ratio of the molar specific activity of the product increment to the molar specific activity of the starting material, in place of $[(n^*/n)/(N_0{}^*/N_0)]$.

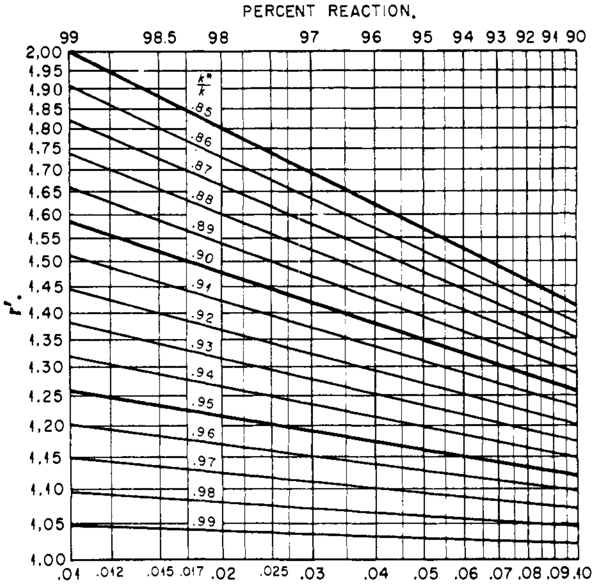

Fig. 3.

(o) The working equation therefore becomes

$$\log r'' = (k^*/k - 1)\log(1 - f) + \log(k^*/k)$$

If a number of incremental product samples collected at different values of f are isotopically assayed, $(k^*/k - 1)$ can be conveniently evaluated as the slope of a plot of $\log r''$ *vs.* $\log(1-f)$. In fact the specific activity of the starting material need not be known; $(k^*/k - 1)$ can be evaluated as the slope of the plot of the logarithm of the incremental product specific activities *vs.* $\log(1-f)$.

(p) Several tests can be applied to equation (o): At 0% reaction, $f = 0$ and $r'' = k^*/k$. As it should be, the molar specific activity of the initial product formed is obtained by multiplying the molar specific activity of the starting material by the ratio of the isotopic rate constants. At 100% reaction, $f = 1$, and $r'' \rightarrow \infty$. This means that all the unlabeled molecules would ultimately react, leaving only a few labeled molecules.

The case where $r'' = 1$ occurs where the molar specific activity of a certain product increment will exactly equal the molar specific activity of the starting material. This "crossing point" occurs at some percentage reaction which depends upon the value of k^*/k. For an average carbon-14 isotope effect having a value of $k_{14}/k_{12} = 0.93$, solution of equation (o) reveals that the "crossing point" occurs at 66% reaction.

(q) At high percentages of reaction, the equation (o) reveals that the specific activity of successive product increments increases very rapidly with increasing values of f. For the average 7% carbon-14 isotope effect referred to above, the product increment formed at 99% reaction has a molar specific activity 28% above that of the starting material.

Figures 4 and 5 show graphically the effect of the value of k^*/k on the variation of r'' with f, the fraction of reaction at which the increment of

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[17] For an example see Gus A. Ropp. C. J. Danby and D. A. Dominey, THIS JOURNAL, **79**, 4944 (1957).

[17a] A. M. Downes, *Aus. J. Sci. Res.*, **A5**, 521 (1952).

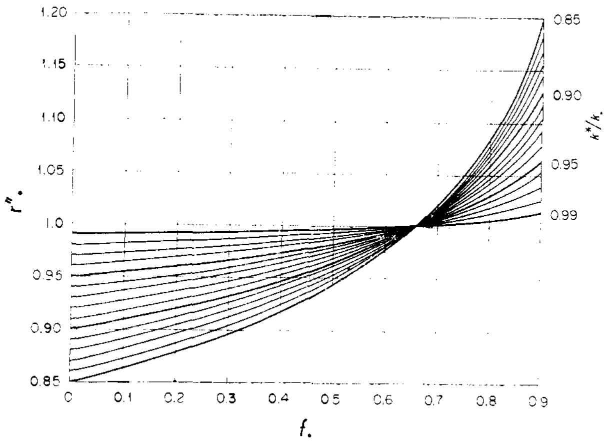

Fig. 4.

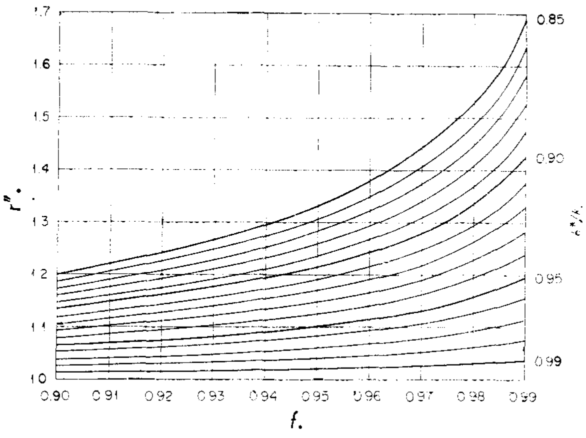

Fig. 5.

product was collected. Figure 4 covers the range 0 to 90% reaction. Figure 5 covers the range 90 to 99% reaction. From Fig. 4 it appears that the "crossing point" referred to in item (p) occurs at about 66% reaction for all the values of k^*/k plotted.*

Deuterium isotope effects are often large enough so that they can be evaluated by comparing the absolute rate for the unlabeled compound with the absolute rate for the pure deuterium labeled compound measured separately.[18]

(4) **Isotope Fractionation in Equilibria and Two Directional Processes.**—As equilibria or two-directional processes frequently occur as part of complex reaction schemes, equilibrium isotope effects are of some interest to the investigator of reaction mechanisms. An example is given later in the present manuscript. In many cases the percentage effect of isotopic substitution on an equilibrium constant can be expected to be less[19] than the percentage effect of a corresponding isotopic substitution on a unidirectional process. The methods of experimentally evaluating equilibrium and rate isotope effects are similar.

(5) **Reaction in an Isotopically-labeled Medium.**—Knowledge about whether a reaction product is isotopically-enriched when the medium in which the reaction is run is isotopically-enriched is frequently helpful as a criterion of a reaction mechanism. Lack of enrichment in the product may, in some cases, disqualify a step or steps in a proposed reaction scheme.

B. **Summary of Isotopic Studies of Decarbonylation Reactions.**—The various applications of isotopes in the study of decarbonylation reactions are outlined in this section. Some of these have been published earlier; others are discussed for the first time in this publication and are therefore described in greater detail in the Experimental section.

(1) **Decarbonylation of Formic Acid in 95–96% Sulfuric Acid.** (a) **Carbon Isotope Effect.**—The temperature coefficient of the carbon-14 isotope effect in the decarbonylation of formic-C^{14} acid has been reported earlier.[20] While the temperature coefficient is subject to some uncertainity, the reported value,[20] $k_{12}/k_{14} = 1.09$ at 25°, is amply accurate enough for purposes of the present paper. Using carbon-13, other workers[21] have reported values of k_{12}/k_{13} which are in reasonable accord with the earlier work[20] with carbon-14. The decarbonylation of formic acid in concentrated sulfuric acid at 25° exhibits a carbon-14 isotope effect which can be considered "large." Few, if any, carbon-14 isotope effects which have been checked in more than one laboratory exceed the value $k_{12}/k_{14} = 1.12$ at 25°.

(b) **Deuterium Isotope Effects in the Decarbonylation of Formic-*d* Acid at 0° and 25°.**—Formic-*d* acid and formic acid were separately decarbonylated under controlled conditions at 0° and 25°. The isotope effect ratios, k_H/k_D, were calculated from the independently measured pseudo-first-order rate constants. Due care was taken to ensure that the stated isotope effects were not merely apparent effects caused by other differences than the isotopic composition of the organic acid.

(c) **Decarbonylation of Formic Acid in Sulfuric Acid Prepared from Oxygen-18-enriched Water.**—Formic acid was decarbonylated in 95.4% sulfuric-O^{18} acid. Both the $H_2SO_4^{18}$ and the 4.6% water, which were enriched equally in oxygen-18, were in large excess compared with the amount of formic acid. The entire sample of carbon monoxide was collected and tested for oxygen-18 enrichment. The extent of enrichment of the original sulfuric-O^{18} acid used was measured by equilibrium with a small sample of carbon monoxide.

(d) **Study of Oxygen-18 Exchange between Carbon Monoxide-O^{18} and 95% to 96% Sulfuric Acid.**—This exchange was found to occur slowly when sulfuric acid was agitated with carbon monoxide-O^{18} at 60°. The oxygen-18-contain-

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* Large scale drawings from which Figures 1, 2, 3, 4, and 5 were taken have been published as a report: Gus A. Ropp, "Curves for Computation of Kinetic Isotope Effects," O.R.N.L.-CF-59-12-4. Requests for copies should be addressed to Laboratory Records Dept., Oak Ridge National Laboratory, P. O. Box "X," Oak Ridge, Tenn.

(18) (a) F. H. Westheimer and N. Nicolaides, THIS JOURNAL, **71**, 25 (1949); (b) K. Wiberg, *Chem. Revs.*, **51**, 730 (1955).

(19) This follows from the method of theoretical calculation of the isotope effects; see (a) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); (b) J. Bigeleisen, *ibid.*, **17**, 675 (1949). The "temperature independent factor" occurs only in rate isotope effect calculations.

(20) Gus A. Ropp, A. J. Weinberger and O. K. Neville, THIS JOURNAL, **73**, 5573 (1951).

(21) R. B. Bernstein, *Science*, **126**, 119 (1957).

ing species in the liquid phase which exchanges may not be sulfuric acid molecules but water molecules in some form present in the concentrated acid.

(e) **Test for Reversibility.**—The reversibility test mentioned in II A (1) was applied to the decarbonylation of formic acid using carbon-14 monoxide.

(2) **Decarbonylation of Benzoylformic Acid in Concentrated Sulfuric Acid.** (a) **Simple Tracer Studies.**—Banholzer and Schmid,[7b] by a simple tracer study using benzoylformic-1-C^{14} acid, demonstrated that the carbon monoxide released contains the label and hence arises from the carboxyl group only.

By the use of benzoylformic-2-C^{14} acid which produced only non-labeled carbon monoxide in the present work, the same conclusion was reached.

(b) **Carbon-14 Isotope Effect with Benzoylformic-1-C^{14} Acid.**—This isotope effect has been reported from another laboratory[22] to have the value k_{12}/k_{14} = *ca.* 1.1. Therefore this carbon-14 effect is of about the same magnitude as that in the decarbonylation of formic acid.

(c) **Carbon-14 Isotope Effect with Benzoylformic-2-C^{14} Acid.**—Benzoylformic-2-C^{14} acid was synthesized by accepted procedures from benzoic-α-C^{14} acid. The isotope effect was evaluated by running the decarbonylation to about one-half completion. Molar specific activities were compared for purified samples representing: (i) the initial acid used, (j) the benzoic-α-C^{14} acid formed upon complete conversion (100% reaction of the benzoylformic-2-C^{14} acid), (jj) the benzoic-α-C^{14} acid produced by partial reaction, (ii) the unreacted benzoylformic-2-C^{14} acid recovered after partial reaction, and (jjj) the unreacted benzoylformic-2-C^{14} acid recovered after partial reaction and quantitatively converted to benzoic-α-C^{14} acid. The isotope effect, k_{12}/k_{14}, was estimated from the measured percentage reaction and the ratios of the various molar specific activities.

(d) **Decarbonylation of Benzoylformic Acid in Sulfuric Acid Prepared from Oxygen-18-enriched Water.**—The method was the same as that used in the parallel experiment with formic acid.

(3) **Decarbonylation of Triphenylacetic Acid in Concentrated Sulfuric Acid.** (a) **Carbon-14 Isotope Effect with Triphenylacetic-2-C^{14} Acid.**—Triphenylacetic-2-C^{14} acid was synthesized by accepted procedures from benzoic-α-C^{14} acid. A sample of the sodium salt was decarbonylated to the extent of about 40% in concentrated sulfuric acid and the reaction was stopped by pouring the solution onto ice and water. Molar specific activities of purified samples representing the following were determined: (i) the initial triphenylacetic-2-C^{14} acid used, (j) the triphenylcarbinol-C^{14} formed by complete reaction, (jj) the triphenylcarbinol-C^{14} formed by partial reaction and (ii) the triphenylacetic-2-C^{14} acid recovered after partial reaction. The isotope effect, k_{12}/k_{14}, was estimated from the measured percentage reaction and the molar specific activity ratios.

(b) **Decarbonylation of Triphenylacetic Acid in Sulfuric Acid Prepared from Oxygen-18-enriched Water.**—This study was run in the same manner as reported for formic acid and benzoylformic acid decarbonylations.

(4) **Isotope Fractionation in the Decarbonylation of Oxalic Acid in Sulfuric Acid.**—Fry and Calvin[23] have reported both the carbon-13 and carbon-14 *intramolecular* isotope effects for the decarbonylation of oxalic acid. Their results appear to be in agreement with earlier results obtained by Lindsay, McElcheran and Thode.[24] The temperature coefficients of the isotope effects were reported,[23] and the temperature coefficient of the carbon-14 isotope effect is of similar magnitude to that reported[20] for formic acid. The authors[23] consider their results to be evidence that carbon–carbon cleavage is not rate determining in the oxalic acid reaction and conclude from this that carbon–oxygen cleavage is probably rate determining. This reaction can be looked at as a decarboxylation reaction as well as a decarbonylation.

III. Experimental

A. **Deuterium Isotope Fractionation in the Decarbonylation of Formic-*d* Acid at 0° and 25°.**—Absolute rates of decarbonylation of formic and formic-*d* acids in excess 96.2% H_2SO_4 at 0.15° and 25.2° were measured using magnetic stirring of the solution in a system similar to that previously described.[20] Evolved carbon monoxide passed through a fritted-glass valve,[25] which maintained a constant pressure over the reaction vessel. The gas was collected over mercury in a bulb where the pressure was measured as a function of time. The synthesis and isotopic assay of the formic-*d* acid azeotrope has been described.[26] To estimate the effect of the method of synthesis of the labeled acid on the rate constant, samples of unlabeled formic acid azeotrope from two sources were used. The samples designated "HCOOH, C.P." consisted of C.P. formic acid diluted to the azeotrope composition with distilled water. The samples designated "HCOOH from NaCN" and "DCOOH from NaCN" were prepared by parallel procedures involving, respectively, hydrolysis and deuterolysis of sodium cyanide. Pseudo-first-order rate constants are reported in Table I. Alkali titrations revealed that the "HCOOH from NaCN" samples had a slightly higher water content than the samples designated "HCOOH, C.P." and "DCOOH from NaCN." The latter samples had the same water content within the limits of the titration error. Hence rates measured with the "HCOOH from NaCN" samples were considered only as controls. The isotope effect ratios were calculated from rate

TABLE I

RATES OF DECARBONYLATION OF FORMIC-*d* ACID AND FORMIC ACID IN 96.2% SULFURIC ACID

Temp., °C.	Acid sample	$10^4 k$, min.$^{-1}$	Mean $10^4 k$	k_H/k_D
0.15	HCOOH, C.P.	64.5	64.0 ± 0.5	1.72
	Duplicate	63.6		
	HCOOH from NaCN	60.5		
	DCOOH from NaCN	36.6	37.2 ± 0.6	
	Duplicate	37.7		
25.2	HCOOH, C.P.	1370	1400 ± 30	1.49
	Duplicate	1430		
	HCOOH from NaCN	1320		
	DCOOH from NaCN	921	939 ± 20	
	Duplicate	957		

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[22] B. Fingerman and R. M. Lemmon, "Isotope Effect in the Decarbonylation of Benzoylformic Acid," Bio-Organic Chemistry Quarterly Report, Dec., Jan. and Feb., 1957–1958, U.C.R.L.-8204.

[23] A. Fry and M. Calvin, *J. Phys. Chem.*, **56**, 897 (1952).

[24] J. G. Lindsay, D. E. McElcheran and H. G. Thode, *J. Chem. Phys.*, **17**, 589 (1949).

[25] O. K. Neville, THIS JOURNAL, **70**, 3501 (1948).

[26] Gus A. Ropp and C. E. Melton, *ibid.*, **80**, 3509 (1958).

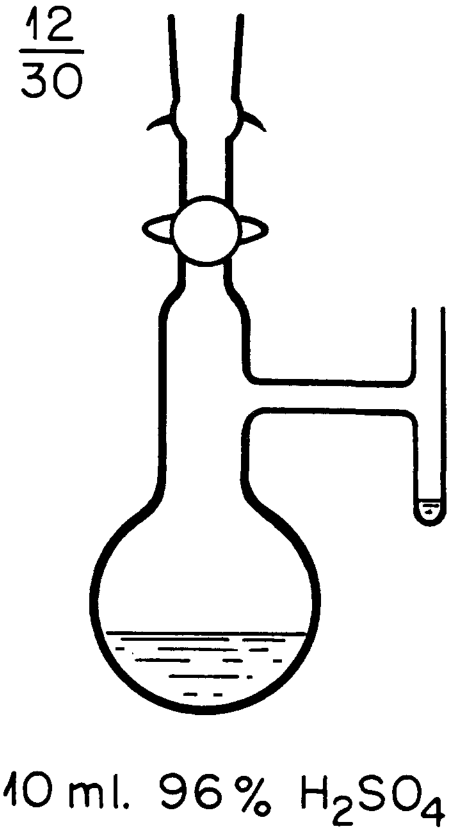

Fig. 6.

constants measured for decarbonylation of the other samples at both temperatures.

In each run a 2.0-ml. sample of formic acid and 137.5-ml. of sulfuric acid were used. In calculating each rate constant, the ***actual measured*** value of the total number of millimoles of gas evolved was used to calculate the number of millimoles of organic acid decomposed. However, in each case the value of the total number of millimoles measured manometrically was in close agreement with the value calculated from the volume and strength of the organic acid used. The first-order kinetic plots invariably were very close to linear only up to about 70% reaction. The slope was always obtained from a line fitted to these points. Above 70% reaction the experimental points deviated more and more from the line, the higher the percentage reaction. The direction of the deviations from the line was always the same and indicated that above 70% reaction the rate was too slow to be explained by the first-order plot. Since the sulfuric acid was in large excess, these deviations from linearity were too large to be accounted for by the slight dilution of the sulfuric acid by the water formed during the reaction.

Two other observations about the general character of the formic acid decarbonylation in excess sulfuric acid are worth recording. First, an initiation period, or delay between the time the formic acid was added to the sulfuric acid and the time the maximum gas evolution rate was reached, was always observed. The delay was much more noticeable at 0° than at 25° and was too long to be explained simply as the time required to mix the formic and sulfuric acids. The delay did not appear to be due to the time required to saturate the sulfuric acid with carbon monoxide since, as has been pointed out previously, the measured total number of millimoles of carbon monoxide agreed with the value calculated from the amount of formic acid decomposed. A second observation suggested that there might be a heterogeneous component of the reaction induced by the glass surface of the vessel; addition of powdered glass to a reaction appeared to cause speeding up of the rate of gas evolution.

B. Decarbonylation of Formic Acid in Sulfuric Acid Prepared from Oxygen-18-enriched Water. (1) **Synthesis of 95.4% Sulfuric Acid from H_2O^{18}.**—Oxygen-18-enriched water and the calculated amount of sulfur trioxide were placed in separate parts of a vacuum line. Each was frozen in liquid nitrogen and evacuated to remove air. The arrangement was such that rotation of the sulfur trioxide bulb about a ground glass taper joint permitted small amounts of liquid sulfur trioxide to be run into the water as desired. The water sample was frozen before the addition of each increment of sulfur trioxide. Reaction occurred when the water container was warmed to room temperature after the addition of each increment of sulfur trioxide. The first few times that warming up was permitted, the reaction was violent and had to be handled carefully. As the strength of the sulfuric acid increased in the water container the successive reactions became less violent. The aqueous sulfuric-O^{18} acid produced had very nearly the oxygen-18 content calculated from the total amount and isotopic composition of the water used and the weight of the sulfur trioxide. Thus complete isotopic equilibrium among all the oxygen atoms in the water and the sulfuric acid was attained.[27]

(2) **A Study of the Exchange of Oxygen-18-enriched Carbon Monoxide with Sulfuric Acid.**—The oxygen-18-enrichment of the above 95.4% $H_2SO_4^{18}$ was determined by exchanging it for 10 days at 60° with a very small sample of commercial grade carbon monoxide and isotopically assaying the carbon monoxide-O^{18} using a mass spectrometer.[28] As the sulfuric-O^{18} acid was in large excess, its isotopic composition was taken to be equivalent to that of the carbon monoxide-O^{18} produced by the exchange reaction. A control experiment demonstrated that the exchange between carbon monoxide and 95 to 96% sulfuric acid should be complete after gentle agitation of the two-phase system at 60° for several days.

The control experiment was performed after quantitatively decomposing a small sample of formic-O^{18} acid by sulfuric acid in the apparatus shown in Fig. 6. The formic-O^{18} acid was frozen in liquid nitrogen in the side tube which was then sealed off at its upper end. Air was removed completely from the system by attachment to a vacuum line at the 12/30 joint and evacuation to 10^{-4} mm. pressure for several hours. The stopcock was closed and the reagents were mixed by tilting the bulb. After the reaction was completed by warming the bulb to 80° for 15 minutes, a mass spectrometric analysis of the gas was performed by simply connecting the 12/30 joint directly to the expansion bulb of the mass spectrometer. Only a small fraction of the gas sample was consumed. The stopcock was closed and the bulb was placed on a slow moving mechanical shaker equipped with an infrared lamp which was in position to heat the sulfuric acid as desired. Table II presents the isotopic analysis of the carbon monoxide after the various successive treatments indicated. The shaker was actually in motion only during the one period indicated. The sample designated COO^{18} represents the initial isotopic composition of the formic-O^{18} acid as it was prepared from that acid by quantitative photochemical oxidation with chlorine gas.[17] The relatively slight changes in the percentage carbon-13 column prove that the steady de-

TABLE II

EXCHANGE OF CARBON MONOXIDE-O^{18} WITH 96.2% SULFURIC ACID

Sample analyzed	Contact time[a] Hot	Contact time[a] Cold	C^{13},[b] %	O^{18}, %
COO^{18}			1.24	1.07
CO^{18}	80°, 15 min.	4 days	1.13	0.54
CO^{18}	80°, 15 min.	4 days	1.12	.49
CO^{18}	60°, 2 hr.	Shaken 60 hr.	1.11	.35
Normal compn.			1.1	.2

[a] Times given are consecutive, not cumulative. [b] The percentage carbon-13 monoxide was estimated using the height of the peak at mass 29, $C^{13}O^{16}$. The mass 29 peak is made up partially of the species $C^{12}O^{17}$, which decreased during the course of the exchange reaction. This explains the slight but steady decrease in the % C^{13} column.

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(27) T. C. Hoering and J. W. Kennedy, THIS JOURNAL, **79**, 56 (1957), have studied the exchange of oxygen-18 between water and sulfuric acid. Their results indicate that this exchange should be rapid at high sulfuric acid strengths.

(28) Thanks are due to W. D. Harmon and John Sites who assayed the carbon monoxide-O^{18} samples.

TABLE III

ISOTOPE FRACTIONATION STUDY OF THE REACTION AT 25°

$$C_6H_5C^{14}OCOOH \xrightarrow{H_2SO_4} C_6H_5C^{14}OOH + CO\uparrow$$

Expt.	Acid assayed	Reaction, %	Sample represents	Activity, mc. per mole	k_{12}/k_{14}
Run 1	Benzoylformic-α-C^{14}	0	Starting acid	1.840 ± 0.013	...
	Benzoic-α-C^{14}	100	Starting acid	1.840 ± .004	...
	Benzoic-α-C^{14}	40	Product	1.802 ± .015	1.029
	Benzoylformic-α-C^{14}	40	Recovd. unreacted starting acid	1.897 ± .017	1.065
Run 2	Benzoic-α-C^{14}	100	Starting acid	1.845 ± .005	...
	Benzoic-α-C^{14}	50	Product	1.805 ± .005	1.031
	Benzoic-α-C^{14}	50	Unreacted starting acid (recovd. and quant. converted to benzoic-α-C^{14} acid)	1.914 ± .002	1.051
			Weighted mean		1.039

crease in the oxygen-18 content was not an apparent effect caused by inward leakage of nitrogen which would steadily increase the mass 28 peak height.

(3) **Decarbonylation in Oxygen-18-enriched Sulfuric Acid.**—A sample of formic acid was decomposed in an excess of the 95.4% sulfuric-O^{18} acid prepared as described in section 1 above. The apparatus was essentially the same as that shown in Fig. 1. The procedure was very nearly the same as that described in section 2 except that the reaction vessel was shaken at room temperature until no more gas was evolved. The carbon monoxide was sampled for mass spectrometric analysis immediately. The percentage oxygen-18 was 0.21% in close agreement with that for a sample of commercial carbon monoxide, 0.20%. The carbon monoxide-O^{18} sample prepared by complete equilibration with the same 95.4% sulfuric-O^{18} acid contained 0.57% oxygen-18. No measurable peak height was found at mass 44, carbon dioxide.

C. Reversibility Test of the Decarbonylation of Formic Acid.—A sample of formic acid was decarbonylated in 96% sulfuric acid at 0° for sufficient time to permit the reaction to proceed to about 50% completion.[20] During the reaction period, carbon-14 monoxide having a specific activity of about 1.0 mc. per mole was bubbled rapidly through the reacting mixture. The reaction was then stopped abruptly by cooling the stirring mixture with liquid nitrogen. The cold mixture was swept for an additional 30 minutes with an inert gas and finally evacuated to remove all gases from the solution.

The purged sulfuric acid was warmed to room temperature and the reaction was allowed to continue. Toward the end of the reaction a large enough sample of evolved gas to fill an ionization chamber was collected and counted using a vibrating reed electrometer.[25] The activity in the chamber was essentially the same as background. The degree of reversibility, if any, of this reaction at 0° was therefore not detectable by the technique described.

D. Decarbonylation of Benzoylformic Acid. (1) Synthesis of Benzoylformic-2-C^{14} Acid.—Benzoylformic-2-C^{14} acid, m.p. 63.5-64.0°, was prepared from benzoyl-α-C^{14} chloride by the methods described in ref. 29. No isotopic dilution was made during or following the synthesis.

(2) **Tracer Study of the Decarbonylation.**—Carbon monoxide produced by decarbonylation of benzoylformic-2-C^{14} acid was swept into an ion chamber with carbon dioxide and counted. No activity above background could be detected. In this, as in almost all of the studies of decarbonylation of organic acids reported in the present paper, the organic acid was stirred with a large excess of concentrated sulfuric acid. The solution was stirred by a glass-enclosed bar magnet as described earlier for decarbonylation of formic acid.[20]

(3) **Isotope Effect in the Decarbonylation of Benzoylformic-2-C^{14} Acid.**—For two individual runs the results are summarized in Table III. The percentage reaction in each case was based on the measured volume of gas evolved when 6.67 mmoles of benzoylformic-2-C^{14} acid was decarbonylated in 70 ml. of 96.2% sulfuric acid. The values of k_{12}/k_{14} reported in Table III were estimated using Figs. 1 and 2. An estimate of an isotope effect ratio based on Fig. 2 is quite sensitive to errors in percentage reaction if the percentage reaction is 60% or less. For this reason, more credence was given to the estimates of k_{12}/k_{14} based on Fig. 1 than to the estimates of k_{12}/k_{14} based on Fig. 2. The mean value, $k_{12}/k_{14} = 1.039$, was obtained by weighting the individual k_{12}/k_{14} ratios by a factor of 2 to 1 in favor of the ratios based on Fig. 1.

Decarbonylation reactions, which used 6.7 mmoles of benzoylformic-2-C^{14} acid and 7 ml. sulfuric acid, were stopped before completion by pouring onto ice. The product, benzoic-α-C^{14} acid, and the unreacted benzoylformic-2-C^{14} acid were separated by the difference in their solubilities in carbon disulfide. The crude benzoylformic-2-C^{14} acid was then treated with charcoal in carbon tetrachloride solution and recrystallized from benzene–ligroin. Crude benzoic-α-C^{14} acid was recrystallized from hot water, then dried and vacuum sublimed at 80° and 2 mm. pressure. All labeled compounds described in this paper were assayed by previously-discussed methods.[30]

(4) **Decarbonylation in Oxygen-18-enriched Sulfuric Acid.**—This study was made in the same way as the analogous study with formic acid. Results were identical with those found with formic acid. No measurable amount of carbon dioxide could be detected in the carbon monoxide.

E. Decarbonylation of Triphenylacetic Acid. (1) Synthesis of Triphenylacetic-2-C^{14} Acid and its Sodium Salt.—Triphenylacetic-2-C^{14} acid was prepared from benzoic-α-C^{14} acid *via* triphenylmethyl-C^{14} chloride[31] by the method described by Shirley.[32] The yields were poorer than indicated[32] there. The sodium salt was prepared as described by Dittmar[5] and stored in a desiccator until used in decarbonylation reactions. No isotopic dilutions were made during or after the synthesis.

(2) **Isotope Effect in the Decarbonylation of Triphenylacetic-2-C^{14} Acid.**—The general method here was the same as that employed in the study of the isotope effect in the decarbonylation of benzoylformic-2-C^{14} acid. However, the sodium salt was used because the free acid dissolves only slowly in sulfuric acid. The mixture of unreacted acid and product carbinol recovered after quenching the 40% reaction with ice was separated by dissolving the acid in boiling 10% sodium hydroxide. The alkaline filtrate was acidified and the recovered triphenylacetic-2-C^{14} acid was recrystallized from aqueous ethanol; Table IV presents the results. A value of $k_{12}/k_{14} \leqq 1.01$ is indicated.

The decarbonylation of triphenylacetic-2-C^{14} acid was carried out as follows: 1.5 mmoles of the sodium salt was slurried with a solution of 2 ml. of water and 11 ml. of 95% sulfuric acid; 30 ml. of a cold mixture of oleum and 95% sulfuric acid was added. After mixing, the strength of the sulfuric acid was 96 to 97%. The use of the cold mixture offset the heat evolved upon mixing, and the solution temperature was 25° at the start of the reaction. The reacting solution was stirred with a bar magnet. The reaction vessel was kept in a bath at 25°.

(3) **Decarbonylation in Oxygen-18-enriched Sulfuric Acid.**—The same procedure was used as with the corresponding studies of formic acid and benzoylformic acid decarbonylations. The 95.4% sulfuric-O^{18} acid solution was also identical in all three cases. However, complete decarbonylation of the triphenylacetic acid produced carbon monoxide-O^{18}

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(29) *Org. Syntheses*, **24**, 14, 16 (1944).

(30) V. F. Raaen and Gus A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

(31) *Org. Syntheses*, **23**, 100 (1943).

(32) D. A. Shirley, "Preparation of Organic Intermediates," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 294.

having 0.30% oxygen-18 as compared with 0.57% oxygen-18 in the carbon monoxide equilibrated with an excess sample of the same 95.4% sulfuric [see III B (3)]. Therefore the enrichment of the carbon monoxide-O^{18} at complete reaction was about 24% of the enrichment of the sulfuric-O^{18} acid employed.

TABLE IV

ISOTOPE FRACTIONATION STUDY OF THE REACTION AT 25°

$$(C_6H_5)_3C^{14}\text{—}COOH \xrightarrow{H_2SO_4} (C_6H_5)_3C^{14}OH + CO\uparrow$$

Compound assayed	Reaction, %	Activity, mc. per mole
Triphenylacetic-α-C^{14} acid	0	1.940 ± 0.005
Triphenylcarbinol-α-C^{14}	100	1.950 ± .010
Triphenylcarbinol-α-C^{14}	40	1.930 ± .004
Triphenylacetic-α-C^{14} (60% recovered unreacted)	40	1.942 ± .007

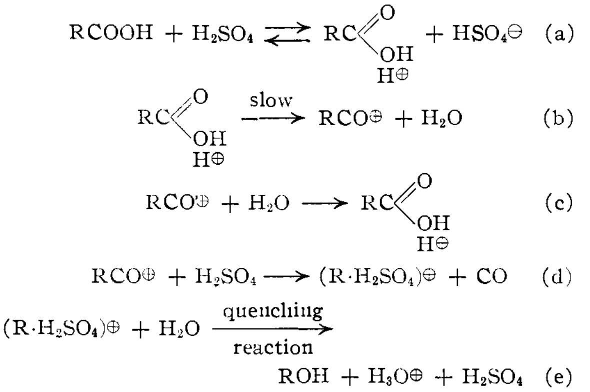
In this run 0.67 mmole of $(C_6H_5)_3C\ COONa \cdot H_2O$ and 10 ml. of 95.4% sulfuric-O^{18} acid were used. Thus the sulfuric-O^{18} acid contained approximately 47 mmoles of water not combined as sulfuric acid. This is a sufficiently large excess of H_2O^{18} so that the interpretation of the results does not depend upon whether or not isotopic equilibration[27] of the H_2O^{18} and $H_2SO_4{}^{18}$ was more rapid than the decarbonylation reaction. Mass spectrometric analysis revealed no measurable amount of carbon dioxide in the carbon monoxide.

(4) **Color of Sulfuric Acid Solutions after Decarbonylation Reactions.**—The relative colors of the reaction mixtures at the end of the reaction and before quenching were: formic acid, almost colorless; benzoylformic acid, pale red; triphenylacetic acid, deeper red.

IV. Discussion of the Results

A. Decarbonylation of Formic Acid.—(1) No evidence was found that the reaction is measurably reversible.

(2) All the evidence is in accord with a general mechanistic scheme like that proposed by Hammett[3c]



$$RCOOH + H_2SO_4 \rightleftarrows RC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown OH}\\H^{\oplus}\end{matrix} + HSO_4^{\ominus} \quad (a)$$

$$RC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown OH}\\H^{\oplus}\end{matrix} \xrightarrow{\text{slow}} RCO^{\oplus} + H_2O \quad (b)$$

$$RCO^{\oplus} + H_2O \longrightarrow RC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown OH}\\H^{\ominus}\end{matrix} \quad (c)$$

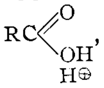
$$RCO^{\oplus} + H_2SO_4 \longrightarrow (R\cdot H_2SO_4)^{\oplus} + CO \quad (d)$$

$$(R\cdot H_2SO_4)^{\oplus} + H_2O \xrightarrow[\text{reaction}]{\text{quenching}} ROH + H_3O^{\oplus} + H_2SO_4 \quad (e)$$

The large carbon-14 isotope effects observed[20] at 0 and 25° are to be expected if step (b), a carbon-14 to oxygen bond cleavage controls the rate. A simplified calculation[33] of the theoretical value can be made considering the 0-point energy effect of the carbon–oxygen bond. Eyring and Cagle[34] and Melander[33] estimated the theoretical values of the isotope effect to be about 12.8% at 0° and 11.9% at 25°. In view of the difficulties involved in experimentally evaluating isotope effects and their temperature coefficients, the agreement of these theoretical values with the corresponding experimental values[20] is reasonably good. However, other cases have been reported in which experimentally determined temperature coefficients of carbon isotope effects were not in close agreement with the theoretically predicted values of the temperature coefficients. The reason is not known.

The lack of oxygen-18 enrichment in the carbon monoxide from the reaction carried out in oxygen-18-enriched sulfuric acid indicates that step (c) in the above mechanistic scheme does not occur in the decarbonylation of formic acid. After the slow process (b), the transfer of a proton to the sulfuric acid (d) is apparently so fast that there is no time for the back reaction (c) of the oxocarbonium ion with water to occur.

As small hydrogen isotope effects, of the order of 50%, were observed in the decarbonylation of formic-*d* acid, it is reasonable to believe that these are merely secondary deuterium isotope effects due to stretching of the carbon-hydrogen bond during the slow step (b). The assumption is that in the activated state one carbon–oxygen bond has been almost completely eliminated while the carbon–hydrogen bond has been stretched relatively little. Quite likely the second carbon–oxygen bond has been shortened in the activated state; this is to say that its character most likely approaches that of the carbon–oxygen bond in carbon monoxide. The fact that all of the bonds in formic acid are probably altered significantly during activation to decarbonylation makes calculation of the absolute theoretical value of any of the rate isotope effects which accompany decarbonylation of carbon-labeled, hydrogen-labeled or oxygen-labeled formic acid extremely hazardous. This is possibly the reason that the theoretically calculated values of the carbon-14 rate isotope effect mentioned above[33,34] do not agree more closely with experimentally measured values[20] at 0 and 25°. This may even explain the lack of better agreement between the theoretical and experimental values of the temperature coefficient of the carbon-14 isotope effect. A more logical approach to the problem of correlating experimental and theoretical values of the rate isotope effects in the decarbonylation of formic acid would be to consider the carbon, hydrogen and oxygen isotope effects not separately but collectively. This is, of course, not yet possible since no method of measuring the kinetic isotope effect in the decarbonylation of formic-O^{18} acid has so far been found.

(3) Before leaving the discussion of isotopic studies of the decarbonylation of formic acid, the oxygen-18 study requires additional comment. Equation (c) in the mechanistic scheme above was eliminated because unenriched carbon monoxide was obtained upon decarbonylation of formic acid in sulfuric-O^{18} acid containing 4.6% oxygen-18-labeled water. The argument is that, had reaction (c) occurred to any appreciable extent, some of the protonated species,  $RC\begin{matrix}{}^{\diagup O}\\{}_{\diagdown OH}\\H^{\oplus}\end{matrix}$, a precursor of carbon monoxide in the proposed scheme, should have been enriched in oxygen-18, and therefore the

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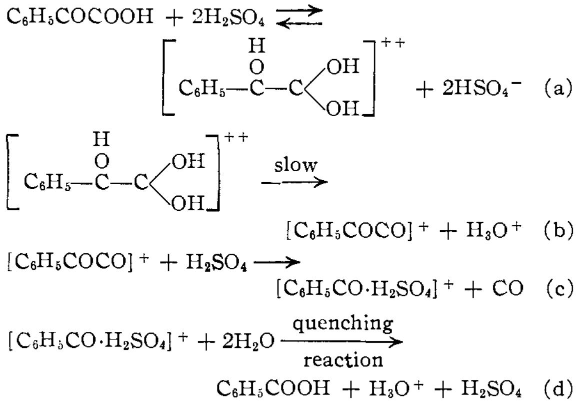
[33] Lars C. S. Melander, "The Use of Nuclides in the Determination of Organic Reaction Mechanisms," University of Notre Dame Press, Notre Dame, Ind., 1955, p. 47.

[34] H. Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 889 (1952).

carbon monoxide should also have been enriched in oxygen-18. It is apparent that this argument is valid only if the two oxygen positions in the species, $\mathrm{RC}\begin{matrix}\diagup\mathrm{O}\\ \diagdown\mathrm{OH}\\ \mathrm{H}^{\oplus}\end{matrix}$, or in the free acid, RCOOH, with which it is in equilibrium, become isotopically equilibrated at a rate which is comparable to the rate of the over-all reaction. However, it is reasonable to expect rapid equilibration of the two oxygens in the carboxyl group of an organic acid dissolved in sulfuric acid through either the rapid ionization to the symmetrical negative ion, $\left[\mathrm{RC}\begin{matrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{matrix}\right]^{\ominus}$, or the rapid equilibration with the symmetrical protonated species, $\left[\mathrm{RC}\begin{matrix}\diagup\mathrm{OH}\\ \diagdown\mathrm{OH}\end{matrix}\right]^{\oplus}$. Experimental evidence for the formation of the symmetrical positive ion from carboxylic acids dissolved in sulfuric acid has been reported recently.[35]

B. Decarbonylation of Benzoylformic Acid.—(1) Clearly, this reaction involves loss of the carbon atom of the carboxyl group as carbon monoxide.

(2) If the mechanism of the decarbonylation of benzoylformic acid is that suggested by Elliott and Hammick[7a]



$$C_6H_5COCOOH + 2H_2SO_4 \rightleftarrows \left[C_6H_5{-}\overset{\overset{\displaystyle H}{\displaystyle O}}{C}{-}C\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}\right]^{++} + 2HSO_4^- \quad (a)$$

$$\left[C_6H_5{-}\overset{\overset{\displaystyle H}{\displaystyle O}}{C}{-}C\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}\right]^{++} \xrightarrow{\text{slow}} [C_6H_5COCO]^+ + H_3O^+ \quad (b)$$

$$[C_6H_5COCO]^+ + H_2SO_4 \longrightarrow [C_6H_5CO{\cdot}H_2SO_4]^+ + CO \quad (c)$$

$$[C_6H_5CO{\cdot}H_2SO_4]^+ + 2H_2O \xrightarrow[\text{reaction}]{\text{quenching}} C_6H_5COOH + H_3O^+ + H_2SO_4 \quad (d)$$

the large isotope effect[22] observed with benzoylformic-1-C^{14} acid is to be expected as a carbon-14 to oxygen bond is cleaved during the slow step (b). Since no enrichment of the carbon monoxide was noted when the decarbonylation was carried out in oxygen-18-enriched sulfuric acid, there is no indication of a back reaction between water and any organic molecule or fragment in the system. This is also in agreement with the proposed reaction mechanism.[7a] No unequivocal interpretation of the observed 3.9% carbon-14 isotope effect in the decarbonylation of benzoylformic-2-C^{14} acid can be made. However, an equilibrium carbon-14 isotope effect of this magnitude on the reversible protonation, step (a), of the α-keto group would not be unreasonable. The principal objection to the reaction scheme as represented by equations (a), (b), (c) and (d) is that it calls for a doubly protonated species or diacidium ion.

C. Decarbonylation of Triphenylacetic Acid.—(1) The mechanism proposed by Deno and Taft[10] is indicated by the equations in section I. If carbon–carbon bond cleavage were rate controlling as they proposed, there should be a measurable isotope effect in the decarbonylation of triphenylacetic-2-C^{14} acid. The observed value of this isotope effect was $k_{12}/k_{14} \leqq 1.01$. This very small value of the kinetic isotope effect definitely does not confirm the Deno and Taft mechanism.

(2) If, as suggested by Deno and Taft,[10] their first step (see section I) were reversible and rapid by comparison with the subsequent carbon–carbon cleavage, carbon monoxide-O^{18} should be formed with a percentage enrichment approaching that of the H_2O^{18} in the 95.4% sulfuric-O^{18} acid used. The experimentally observed enrichment of the carbon monoxide-O^{18}, about 24% of the enrichment of the H_2O^{18} in the 95.4% sulfuric-O^{18} acid used, also fails to confirm the Deno and Taft mechanism. The 24% enrichment of the carbon monoxide-O^{18} can, however, be explained by assuming a decarbonylation mechanism which is intermediate between the Hammett mechanism for formic acid decarbonylation and the other extreme proposed by Deno and Taft.[10] The assumed mechanism can be best described in terms of the reactions (a) to (e) of section IV A (2). If R is the triphenylmethyl group, reaction d is the attack of sulfuric acid on the hindered number 2 carbon and is understandably much slower than the corresponding proton transfer to sulfuric acid in the case of the formic acid decarbonylation (R = H). Therefore in the triphenylacetic acid decarbonylation, reaction (c) can compete much more favorably with reaction (d) than is possible in the formic acid decarbonylation. Hence some enrichment of the carbon monoxide takes place *via* reaction (c) during the triphenylacetic acid decarbonylation in oxygen-18 enriched sulfuric acid. The observed partial enrichment of the carbon monoxide-O^{18}, however, indicates that (c) is probably slightly slower than (d). The relative rates of (c) and (d) should be a function of the percentage water in the sulfuric acid. This suggests the possibility of additional experimental checks on the assumed mechanism. The degree of enrichment of the carbon monoxide-O^{18} could be determined as a function of the percentage water in the sulfuric-O^{18} acid.

The intermediate character of the mechanism assumed here for the decarbonylation of triphenylacetic acid may account for the observed nonintegral slope[7a] of the plot of log *k* *vs.* H_0 observed for the reaction.

However, another possibility should not be overlooked, namely, that the 24% enrichment of the carbon monoxide-O^{18} formed during decarbonylation of triphenylacetic acid in enriched aqueous sulfuric acid may be merely the result of a side reaction. Indeed, this seems to be a reasonable possibility in view of the very low carbon-14 isotope effect found during decarbonylation of triphenylacetic-2-C^{14} acid. If the observed 24% enrichment of the carbon monoxide-O^{18} were due merely to some side reaction between triphenylacetic acid and the sulfuric acid medium, there

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(35) R. Stewart and K. Yates, "Position of Protonation of the Carboxyl Group. Basicity of Substituted Acetophenones and Benzoic Acids," Paper 77 presented to the Organic Division, American Chemical Society, San Francisco, Calif., April 16, 1958.

would be no reason—except for the somewhat questionable interpretation of acidity function relationships—to believe that the mechanism of decarbonylation of formic and triphenylacetic acids are dissimilar.

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OAK RIDGE, TENN.

[CONTRIBUTION NO. 556 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Methoxydifluoromethyl Isocyanate by Thermal Cleavage of a Diazetidine

BY J. C. KAUER AND A. K. SCHNEIDER

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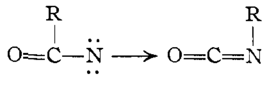
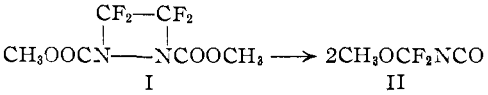
Dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidine-1,2-dicarboxylate pyrolyzes with the migration of a methoxyl group to yield methoxydifluoromethyl isocyanate in over 70% yield. Some of the reactions and properties of this material are described.

Rearrangements are involved in a number of well-known syntheses of isocyanates. Thus, in the Hofmann, Lossen and Curtius reactions, alkyl or aryl groups migrate from the carbon atom of a carbonyl group to an adjacent univalent nitrogen atom.[1]



$$O{=}\overset{R}{\underset{}{C}}{-}\ddot{\underset{\cdot\cdot}{N}} \longrightarrow O{=}C{=}\overset{R}{N}$$

We wish to report the synthesis of an isocyanate by a rearrangement involving the migration of a methoxyl group. Dimethyl 3,3,4,4-tetrafluoro-1,2-diazetidine-1,2-dicarboxylate (I) was prepared in 47% yield by the thermal addition of tetrafluoroethylene to dimethyl azodicarboxylate. Methoxydifluoromethyl isocyanate (boiling point, 44°) (II) was obtained in over 70% yield by the passage of this ester at 5 mm. pressure through a quartz-packed tube heated to 600°.

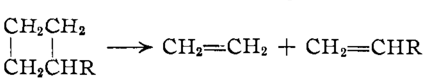


I II

$$CH_3OOC\underset{|}{N}{-}\underset{|}{N}COOCH_3\ (\overset{CF_2-CF_2}{}) \longrightarrow 2CH_3OCF_2NCO$$

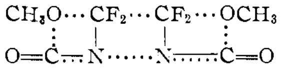
Although the elemental analysis of the product was the same as that of the diazetidine ester I, the molecular weight was just one-half. A strong infrared absorption at 2270 cm.$^{-1}$ and the lack of absorption at 1600–1800 cm.$^{-1}$ indicated that an isocyanate rather than an ester function was present in the molecule.

Although the thermal cleavage of diazetidines has not previously been reported, the analogous reaction is well known in the cyclobutane series.[2]



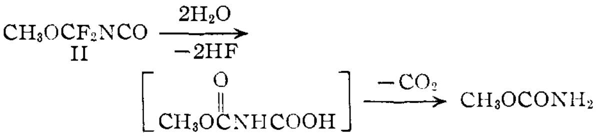
$$\begin{matrix}CH_2CH_2\\ |\quad\ |\\ CH_2CHR\end{matrix} \longrightarrow CH_2{=}CH_2 + CH_2{=}CHR$$

A similar cleavage has been reported for the fluorinated cyclobutanes.[3] These homogeneous reactions exhibit first-order kinetics and do not appear to be radical chain reactions.[2] For the pyrolysis of I a concerted reaction involving a transition state such as III is a reasonable explanation of the formation of the isocyanate.



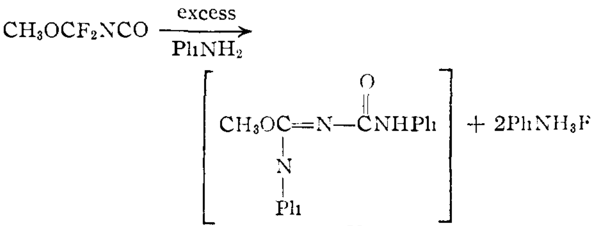
III

It is known that the difluoromethylene group adjacent to an isocyanate function is extremely sensitive to nucleophilic attack.[4,5] Methoxydifluoromethyl isocyanate reacted vigorously with water to form methyl carbamate.



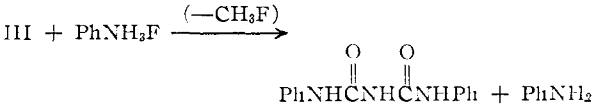
$$\underset{II}{CH_3OCF_2NCO} \xrightarrow[-2HF]{2H_2O} \left[CH_3O\overset{O}{\overset{\|}{C}}NHCOOH\right] \xrightarrow{-CO_2} CH_3OCONH_2$$

Methyl carbamate was also isolated from the reaction of II with methanol. Aniline reacted with the isocyanate II to form diphenylbiuret, possibly through the intermediate formation of the amidine IV. A similar reaction has been reported for perfluoropropyl isocyanate and ammonium hydroxide.[5]



IV

$$CH_3OCF_2NCO \xrightarrow[PhNH_2]{excess} \left[CH_3O\underset{\underset{Ph}{|}}{\underset{N}{\underset{|}{C}}}{=}N{-}\overset{O}{\overset{\|}{C}}NHPh\right] + 2PhNH_3F$$



$$III + PhNH_3F \xrightarrow{(-CH_3F)} PhNH\overset{O}{\overset{\|}{C}}NH\overset{O}{\overset{\|}{C}}NHPh + PhNH_2$$

Acid cleavage of IV to form diphenylbiuret has been reported.[6]

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 497 ff.

[2] (a) C. T. Genaux, F. Kern and W. D. Walters, THIS JOURNAL, **75**, 6196 (1953); (b) M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, *ibid.*, **76**, 6271 (1954).

[3] (a) J. L. Anderson, U. S. Patents 2,733,278 (1956); (b) 2,773,089 (1956).

[4] (a) R. L. Dannley and M. Lukin, *J. Org. Chem.*, **21**, 1036 (1956); (b) R. L. Dannley, R. G. Taborsky and M. Lukin, *ibid.*, **21**, 1318 (1956); (c) R. L. Dannley, R. G. Taborsky and M. Lukin, Abstracts of Papers, 130th American Chemical Society Meeting, Atlantic City, N. J., September 16–21, 1956, p. 26-O; (d) R. L. Dannley, D. Yamashiro and R. G. Taborsky, Abstracts of Papers, 134th American Chemical Society Meeting, Chicago, Ill., September 7–12, 1958, p. 38-P.

[5] A. H. Ahlbrecht and D. R. Husted, U. S. Patent 2,617,817 (1952).

[6] R. H. McKee, *Am. Chem. J.*, **26**, 233 (1901).