lithium aluminum hydride and 3 mol of *tert*-butyl alcohol.[1]

GLC Analyses. GLC analyses were carried out by using a Varian Model 1200 FID Chromatograph fitted with stainless-steel columns.

Reaction of LTBA with Triethylborane in Tetrahydrofuran. A 100-mL flask with a septum inlet, thermometer well, and a magnetic stirring bar was connected to a mercury bubbler, and the apparatus was purged with nitrogen. The flask was immersed in a water bath (ca. 25 °C) and LTBA (33.2 mL, 20 mmol of a 0.6 M solution in THF) was placed in the reaction flask followed by 4 mL (8 mmol) of a 2 M solution of *n*-dodecane in THF (internal standard). To this well-stirred mixture, triethylborane, 2.84 mL (20 mmol), was added. A vigorous and exothermic reaction ($\sim$45 °C) was observed. After 5 min, 4 mL of the reaction mixture was withdrawn and hydrolyzed with water and the hydrogen evolved measured. There was present only 28% of the residual hydride (based on the original hydride concentration). Simultaneously, another minute sample was withdrawn, hydrolyzed, and analyzed for the 1-butanol formed by GLC on a Carbowax 20M 6 ft $\times$ $^1/_8$ in. column. There was present 73% of 1-butanol. The reductive cleavage was essentially complete in 3 h.

Another reaction was carried out by utilizing only a catalytic quantity of triethylborane (10 mol %). The results are summarized in Figure 1.

Reaction of LTBA with Triethylborane in Diethyl Ether. A typical reaction setup was assembled. Commercial LTBA, 2.54 g (10 mmol), was introduced into the reaction flask. Diethyl ether, 18.6 mL, was introduced into the reaction flask and the mixture stirred well. LTBA remains insoluble in ether. To this well-stirred solution, 1.42 mL (10 mmol) of triethylborane was introduced. No visible change was observed. Another identical reaction (blank) was conducted in which instead of triethylborane 1.42 mL of diethyl ether was added. After 1 h, both mixtures were hydrolyzed with water, and the hydrogen evolved was measured with a gas buret, connected to the system through a dry-ice trap. There was present 95% of the originally introduced active hydride in the reaction mixture.

Reaction of LTBA–Triethylborane with 7-Oxabicyclo-[2.2.1]heptane in THP. A typical reaction setup was assembled. In the flask was placed 2.54 g (10 mmol) of LTBA and 2.6 mL

of THP. The flask was immersed in a water bath (ca. 25 °C). Then 0.5 mL of a 5.0 M solution in THP of 7-oxabicyclo-[2.2.1]heptane (2.5 mmol) was injected into the reaction flask, followed by 0.5 mL of a 2.0 M solution in THP of *n*-tridecane (1 mmol) to serve as an internal standard, followed by 1.42 mL of triethylborane (10 mmol). The mixture was stirred vigorously. After 1 h, 0.5 mL of the reaction mixture was withdrawn with a syringe and quenched with a mixture of water and ether. The aqueous phase was saturated with anhydrous potassium carbonate. GLC analysis of the dry ethereal layer revealed the presence of 91% of cyclohexanol. In 3 h, a 97% yield of cyclohexanol was realized.

Reaction of LTBA–Triethylborane with 2,5-Dihydrofuran. A typical reaction setup was assembled. LTBA (2.8 g, 11 mmol), was placed in the reaction flask followed by 6.6 mL of THP. 2,5-Dihydrofuran (1 mL of a 5 M solution in THP, 5 mmol) was introduced into the reaction flask followed by 1 mL of a 2 M solution of *n*-tridecane in THP (2 mmol) to serve as an internal standard. To this well-stirred mixture, triethylborane, 1.42 mL (10 mmol), was added. The reaction was monitored periodically by GLC. In 2 h, there was realized a 95% yield of pure *cis*-crotyl alcohol.

Another reaction carried out by using a catalytic quantity of triethylborane (10 mol %) yielded *cis*-crotyl alcohol in 91% yield in a 24-h period.

(14) Available from Aldrich Chemical Co., Inc., Milwaukee, Wis. 53233.

Carbon Isotopic Fractionation in the Schmidt Decarboxylation: Evidence for Two Pathways to Products

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The evolution of CO_2 at 5 ± 2 °C from the H_2SO_4-catalyzed reaction of *n*-octanoic acid with HN_3 in $CHCl_3$ (the Schmidt decarboxylation) takes place in two kinetic phases with different carbon kinetic isotope effects. Experiments were carried out under high-efficiency stirring conditions at HN_3 concentrations ranging from 1.47 to 0.24 M. At an initial HN_3 concentration of 1.47 M, the pseudo-first-order rate constant for the first kinetic phase was 0.07 ± 0.03 h^{-1}, with $^{12}k/^{13}k$ = 1.0589 ± 0.0003. After a lag time of 48 min the rate of CO_2 evolution changed, with the pseudo-first-order rate constant (1.47 M HN_3) increasing to 0.45 ± 0.02 h^{-1}; $^{12}k/^{13}k \approx 1.03$. Results obtained at lower HN_3 concentrations showed that the first, slower reaction phase displayed overall first-order kinetics, its rate being independent of HN_3 concentration. The first reaction phase could be suppressed by addition of $KHSO_4$ to the H_2SO_4. Preequilibration of the $HN_3/CHCl_3$ with H_2SO_4 markedly affected the isotopic composition of the initial CO_2 product, apparently effecting the initial transient utilization of the second-phase reaction pathway through the action of the H_2SO_4 on the HN_3. Although the kinetic phases could not be resolved at 22 °C, the isotopic composition of the evolved CO_2 indicated that both pathways to the product were being utilized.

The reaction between hydrazoic acid and carbonyl compounds is known as the Schmidt reaction. When the carbonyl compound is a carboxylic acid, attack of HN_3 is followed by rearrangement and decarboxylation as indi-

cated in eq 1.[1,2] Despite the fact that this reaction is a

$$RCH_2CO_2H + HN_3 \rightarrow RCH_2NH_2 + CO_2 + N_2 \quad (1)$$

well-known example of a rearrangement involving mi-

gration to an electron-deficient nitrogen,[3] there is considerable disagreement in the literature as to the details of the mechanism.[3-8] Furthermore, it has been reported that groups other than the carboxyl carbon can be oxidized under the vigorous conditions of the Schmidt decarboxylation.[9]

Our interest in this reaction grew from a desire to have a one-step decarboxylation technique that was so well characterized and reproducible that the carbon dioxide produced could be used to determine the $^{13}C/^{12}C$ ratio in the carboxyl group in n-alkanoic acids (C_2–C_{30}) with a relative standard deviation of 0.1% or better (e.g., $^{13}C/^{12}C$ = 0.010 90 ± 0.000 01). Variations in the $^{13}C/^{12}C$ ratio frequently exceed 1% when different natural carbon pools ("organic" vs. "inorganic" carbon in sediments, lipids vs. carbohydrates, etc.) are examined.[10] Interpretations of these variations, which are due to isotopic fractionations accompanying biochemical and geochemical processes, have been extremely useful in elucidating broad aspects of the carbon cycle. We wish now to extend this approach to the study of molecular transformations in nature and, accordingly, require techniques applicable to intramolecular isotopic analyses. With this goal in mind, we have carried out kinetic and isotopic investigations of the Schmidt reaction as applied to n-alkanoic acids, searching for ways in which the reaction can be driven absolutely to completion without the imposition of side reactions and carefully measuring the isotopic fractionations encountered during the course of the reaction.

Our investigations have revealed that at low temperatures (5 °C) the Schmidt reaction displays two kinetic phases characterized by different pseudo-first-order rate constants *and* by different carbon kinetic isotope effects. At high temperatures (22 °C), the kinetic distinctions are blurred, but carbon isotopic analyses still indicate that two different kinetic isotope effects are controlling the isotopic composition of the product. It thus appears that two pathways link the reactants and products when the Schmidt reaction is applied to carboxylic acids. We have exploited our observations in order to develop an accurate carbon isotopic analytical procedure[11] and will concentrate in the future on applications of that procedure rather than on the mechanistic studies which these observations clearly suggest. It is our hope that this report can represent a useful contribution to further studies of the Schmidt reaction.

Results

Experimental Approach. Our requirement that the Schmidt reaction be made applicable to the isotopic analyses of micromole quantities of carboxylic acids suggested a number of procedural innovations. First, we found that the usual procedure,[6,9,12] in which HN_3 is

generated in situ by reaction between H_2SO_4 and NaN_3, inevitably produced a large CO_2 blank which was ultimately traced to some CO_2-releasing impurity present in the NaN_3. To avoid this problem, we have introduced HN_3 directly, using a carefully degassed solution of HN_3 in $CHCl_3$. Coincidentally, the HN_3 concentration in this solution can be accurately standardized, providing an important control over the uniformity of reaction conditions. Second, experience with other procedures in isotopic analysis has strongly indicated the advantages of carrying out reactions in sealed tubes, simultaneously simplifying product recovery and minimizing contamination of the reaction system. To gain these advantages, we sealed the reactants ($HN_3/CHCl_3$, RCO_2H, and H_2SO_4) in an evacuated tube and mixed them under vacuum. When the progress of the reaction under a given set of conditions was to be followed, multiple tubes were prepared and opened at intervals. Finally, the presence of the H_2SO_4 catalyst as a separate phase in the reaction mixture creates a situation in which the progress of the reaction can depend not only on the kinetic characteristics of the reaction itself but also on rates of mass transfer of reactants and products to and from the catalyst. To minimize these effects, we have provided highly efficient stirring by employing a vortex mixer to agitate the reaction tube, producing a uniform, extremely fine dispersion of H_2SO_4 in the $CHCl_3/HN_3$ phase.

The reaction temperature employed in this work was 5 °C, in spite of the fact that Schmidt decarboxylations of n-alkanoic acids are usually carried out at a temperature of at least 40 °C.[9,12-14] This relatively low temperature was chosen in order to allow more careful studies of the initial stages of the reaction and in order to minimize,[15] if not eliminate entirely,[16] H_2SO_4-catalyzed degradation of the HN_3, a process which might otherwise complicate the results of the kinetic investigations.

Kinetic and Isotopic Observations. Determinations of the amounts of CO_2 in the reaction tubes opened at various total reaction times provided kinetic information which was crude but useful in the context of interest. Hydrazoic acid was present in substantial excess, and the rate of evolution of CO_2 could often be described by a pseudo-first-order rate expression having the form

$$-\ln (1 - f) = kt \qquad (2)$$

where f is the fractional yield of CO_2 ($0.0 < f < 1.0$), t is the elapsed time, and k is the experimentally determined pseudo-first-order rate constant.

The isotopic composition of the isolated and purified CO_2 product was measured directly and is reported here in terms of $\delta^{13}C_{PDB}$, where $\delta^{13}C_{PDB} = [(R_{sample}/R_{PDB}) - 1]10^3$, $R = {}^{13}C/{}^{12}C$, and PDB indicates the Pee Dee Belemnite isotopic standard ($R_{PDB} = 0.011\,237\,2$).[17] The kinetic isotope effect prevailing at the carboxyl carbon was calculated by using eq 3. This expression has been recast

$$\left(\frac{{}^{13}k}{{}^{12}k} - 1\right) \log (1 - \alpha f) =$$

$$\log \left[1 + \left(\frac{\delta_{Ro} - \delta_{Pf}}{\delta_{Ro} + 10^3}\right)\left(\frac{\alpha f}{1 - \alpha f}\right) \right] \qquad (3)$$

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Table I. Summary of Experimental Conditions, Rate Constants, and Isotope Effects

	initial conditions[a]		observed results[b]			
trial	[HN$_3$], M	[RCO$_2$H], M	k_I, h^{-1}	t_{II}, min	k_{II}, h^{-1}	$^{12}k_I/^{13}k_I$
A	1.52	0.099 ± 0.001	>0.15 (2)			
B	1.467 ± 0.004	0.103 ± 0.005	0.07 ± 0.03 (5)	48 ± 9	0.45 ± 0.02 (5)	1.0588 ± 0.0004 (5)
C	1.467 ± 0.004	0.191 ± 0.001	0.06 ± 0.02 (6)	~75	~0.45	1.0593 ± 0.0011 (5)
D	0.82 ± 0.02	0.099 ± 0.001	0.07 ± 0.001 (8)[d]	43 ± 15[d]	0.23 ± 0.02 (4)[d]	1.058 ± 0.001 (7)
E[c]	0.82 ± 0.02	0.099 ± 0.001	0.06 ± 0.01 (5)			see Figure 2
F[e]	0.82 ± 0.02	0.099 ± 0.001		12 ± 5	0.25 ± 0.02 (8)	
G[f]	0.82 ± 0.02	0.098 ± 0.001		14 ± 10	1.27 ± 0.16 (5)	
H	0.241 ± 0.002	0.098 ± 0.001	0.0064 ± 0.0005 (5)			1.057 ± 0.0003

[a] All reactions carried out at 5 ± 2 °C unless otherwise noted. The first-order rate constant for HN$_3$ decomposition in this system is 0.033 ± 0.001 h^{-1} (see ref 11). [b] Parenthesized numbers indicate numbers of points used in deriving the tabulated values. Indicated uncertainties are ±1 standard deviation. [c] HN$_3$/CHCl$_3$ equilibrated with concentrated H$_2$SO$_4$ for 1 h prior to reaction. [d] Reaction phases deduced from isotopic fractionations; see text. [e] H$_2$SO$_4$ saturated with KHSO$_4$. [f] T = 22 ± 1 °C.
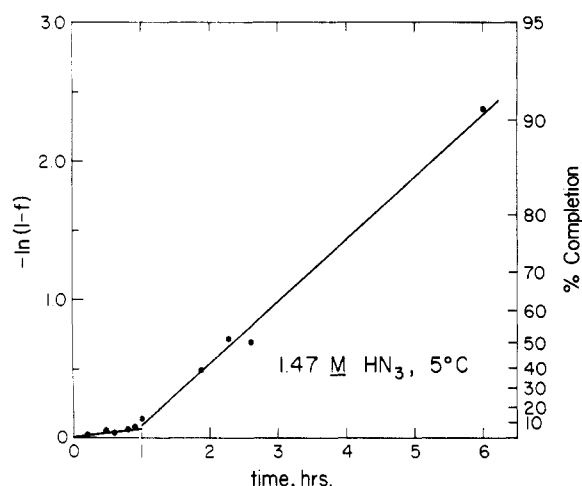

Figure 1. Linearized kinetic data (eq 2 and 4) representing trial B in Table I. The slopes of the linear segments are given by k_I and k_{II}; t_{II} is the t-axis intercept of the second linear segment.

in the δ notation from the derivation by Bigeleisen and Wolfsburg.[18] The isotopic rate constants are noted as ^{13}k and ^{12}k, f denotes the fractional yield (0.0 < f < 1.0), and the δ terms denote isotopic compositions expressed as $\delta^{13}C_{PDB}$ values, with Ro designating the initial reactant and Pf designating the pooled product at a given degree of reaction completion. The coefficient α is a correction factor taking into account the finite abundance of the "tracer" (^{13}C) isotope. Its value depends on the isotopic composition of the reactant, the pooled product, and the isotopic standard and is given in this case by α = (101 124 + 1.124δ_{Ro})/(101 124 + 1.124δ_{Pf}).

Summary of Results. The kinetic results obtained under one particular set of reaction conditions are shown in Figure 1 and can be used to introduce a summary of all experimental results. It is evident that two reaction "phases" can be observed. Both phases (hereafter termed I and II) display pseudo-first-order kinetics, the second after a lag time which can be determined by fitting a line using the expression given in eq 4, where k_{II} is the

$$-\ln (1 - f) = k_{II}(t - t_{II}) \qquad (4)$$

pseudo-first-order rate constant applicable to phase II and t_{II} is the lag time. Quantitative information pertaining to the data in Figure 1 is summarized, together with similar information for a variety of reaction conditions, in Table I. The entry relevant to Figure 1 is noted as trial B. Unless otherwise noted, all reactions were carried out at 5 ± 2 °C.

(18) J. Bigeleisen and M. Wolfsburg, Adv. Chem. Phys., 1, 15 (1958).

Table II. Carbon Isotopic Compositions and Apparent Kinetic Isotope Effects for Trial B

f	t, h	δ_{Pf}, ppt[a]	$^{12}k/^{13}k$[b]
0.0093	0.20		
0.0297	0.60	-103.87 ± 0.10[c]	1.06021[d]
0.0480	0.47	-101.65 ± 0.06[c]	1.05811[d]
0.0567	0.80	-101.75 ± 0.11[c]	1.05850[d]
0.0715	0.90	-101.10 ± 0.47[c]	1.05818[d]
0.1262	1.00	-100.28 ± 0.23	1.05897[d]
0.3887	1.87	-83.72 ± 0.29	1.04649
0.4993	2.60	-84.42 ± 0.22	1.05297
0.5090	2.28	-83.68 ± 0.23	1.05232
0.9069	6.00	-58.10 ± 0.10	1.03174

[a] Parts per thousand. [b] Kinetic isotope effects calculated from eq 3 and δ_{Ro} = -50.72 ± 0.04. [c] Tabulated value of δ_{Pf} has been corrected for background contributions (see ref 11 for discussion). [d] Value use to calculate the average phase I KIE (=1.0588 ± 0.0004 (6)).

The isotopic composition of the CO$_2$ product observed in each of the runs in trial B is shown in Table II. Entries in the last column in Table II represent the kinetic isotope effect (KIE) required to account for the observed carbon isotopic fractionation. When a single isotope effect prevails throughout the course of a reaction and when there are no side reactions affecting either the substrate or the product, the insertion of a single value of $^{12}k/^{13}k$ in eq 3 will serve to relate δ_{Pf} and δ_{Ro} for all values of f. This is exemplified by the first six tabulated values of $^{12}k/^{13}k$, which are identical within experimental uncertainties and which yield an average KIE of 5.88 ± 0.04%. As the reaction proceeds to higher yields, however, the calculated $^{12}k/^{13}k$ values become far less reproducible and drift toward lower values. The onset of this drift (marked arbitrarily by a vertical space in Table II) correlates perfectly with the onset of phase II in the kinetic data, and we conclude that a reaction pathway characterized by a different carbon kinetic isotope effect becomes available at this time.

While the KIE associated with phase I can be accurately and precisely measured, the value of $^{12}k/^{13}k$ associated with phase II is far less accessible. It is clear that it must be *less* than that of phase I ($^{12}k/^{13}k$ entries in Table II tend to lower values) and on the basis of the longest reaction time—to which the phase II pathway has made by far the largest contribution—that it might be as low as 1.032. However, a number of cautionary statements are in order. First, calculated $^{12}k/^{13}k$ values become appreciably less precise at f > 0.6,[18] where δ_{Pf} is a relatively steep function of f and where uncertainties in the measurement of f can, accordingly, introduce significant uncertainties in $^{12}k/^{13}k$. Second, the observation that the trend of $^{12}k/^{13}k$ values is not monotonic indicates that there is some tube-to-tube irreproducibility in the onset of phase II. (Indeed, the signs

and magnitudes of the observed isotopic fluctuations indicate that this same factor is probably responsible for most of the scatter observed in the kinetic data.) Finally, any attempt to recover $^{12}k_{II}/^{13}k_{II}$ from the observed isotopic compositions runs into a serious problem of model dependency: on the one hand, it could be assumed that phase I "shut off" when phase II started; on the other hand, it could be assumed that phase II was actually a hybrid, with products being produced simultaneously by two reaction pathways. The functional relationships between δ_{Pf} and f calculated on the basis of either of these assumptions differ significantly, but the irreproducibility cited above is just great enough to prevent the confident choice of both an appropriate model and a correct $^{12}k_{II}/^{13}k_{II}$ value. It appears most useful, then, to consider the effects associated with changes in the reaction conditions.

While the entries in Table I are, for the most part, self-explanatory, some commentary is useful. Trial C duplicated B except that the organic acid concentration was doubled. The results similarly duplicate those of trial B except for a marked extension of the lag time preceding phase II. The transition between phases appeared to be particularly smooth, curvature in the kinetic plot being so marked that the value of k_{II} had to be estimated from only two points. Trial D duplicated B except that the initial concentration of hydrazoic acid was reduced. In this case, the irreproducibility in the onset of phase II, noted previously to a small extent at the higher concentration of HN_3, became extreme. Seven tubes opened at relatively low yields gave $^{12}k/^{13}k$ values between 1.055 and 1.061 and appeared, therefore, to have followed only the phase I pathway. Four other tubes gave higher yields coupled with $^{12}k/^{13}k$ values between 1.037 and 1.045 even though the reaction times exceeded those of the "pure phase 1" tubes in only one of the four cases. Remarkably, when the isotopic data were used to assign the tubes to either phase I ($^{12}k/^{13}k \geq 1.055$) or phase II ($^{12}k/^{13}k \leq 1.045$) for kinetic calculations, the values derived for k_I and t_{II} corresponded with those observed in trials B and C, and k_{II} was found to be reduced by a factor of 2.0, in rough agreement with the factor of 1.8 expected if the rate of phase II had a first-order dependence on the HN_3 concentration. Further reductions in the concentration of HN_3 (trial H) resulted in a greatly decreased reaction rate and no change in the observed kinetic isotope effect.

It was observed that the kinetic results obtained at these reactant concentrations could be greatly simplified, with phase I being almost completely suppressed if the H_2SO_4 was saturated with $KHSO_4$ prior to the reaction (trial F). In this case, (i) k_{II} was decreased by exactly a factor of 1.8, (ii) the lag time was very significantly reduced, though not eliminated, and (iii) the isotopic compositions observed corresponded to $^{12}k/^{13}k$ values between 1.032 and 1.053. Considering these observations in sequence, it can be concluded that the rate of phase II does have a first-order dependence on the concentrations of both HN_3 and organic acid (i), together with similar observations in trial D, that the two reaction pathways are in competition for some reactant, intermediate, or catalyst (ii), and that the elimination of the phase I reaction pathway was not complete, though it can again be noted that $^{12}k_{II}/^{13}k_{II}$ might be on the order of 1.03 (iii).

Preequilibration of the HN_3 solution with the H_2SO_4 catalyst (trials A and E) affected both the initial reaction rate and the isotopic composition of the resulting product. Both effects were very short-lived, the increased rate being noticeable only at high concentrations of HN_3 (trial A). At lower concentrations (trial E) the effect on the rate was
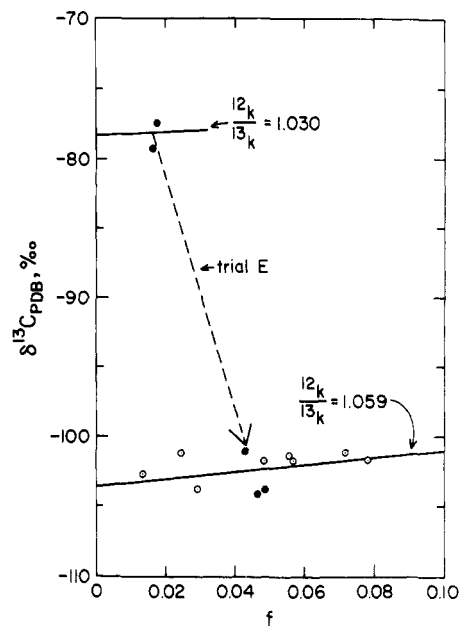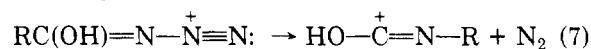

Figure 2. Isotopic composition of product CO_2 as a function of yield for trials E (filled circles), B, and C. The latter trials (open circles), in which the HN_3 was not preequilibrated with H_2SO_4, follow the relationship expected (eq 4; solid line) when a single isotope effect is controlling the isotopic composition of the product.

barely perceptible, but two tubes opened very soon after the mixing of the reactants gave remarkable isotopic compositions (Figure 2) corresponding to $^{12}k/^{13}k = 1.030$. It has already been shown that phase II is characterized by a rate significantly greater than that of phase I and by a kinetic isotope effect at least as small as, but possibly near, 1.032 (trials B and F). Therefore, the observations of trial E suggest that the preequilibration causes the transient initial utilization of the reaction pathway unique to phase II but that this pathway cannot be self-sustaining at this stage of the reaction.

The effect of increasing the reaction temperature can be observed in trial C. Although two kinetic phases could not be resolved at room temperature, it appears likely that both reaction pathways were utilized inasmuch as (i) a least-squares analysis of the kinetic data gave a finite, though statistically insignificant, value for t_{II} and (ii) the calculated kinetic isotope effect did vary significantly with yield, decreasing from 1.051 at low yield to 1.038 at high yield.
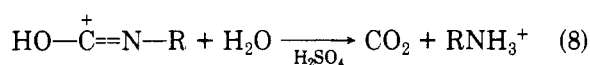
Discussion

The mechanism of the Schmidt reaction involving carboxylic acids has not been definitely established, although only two principal alternatives can be discerned among the possibilities discussed. On the one hand, it has been suggested[3,6,8,19-21] that the reaction proceeds by way of an acylium ion, formation of which controls the rate of the reaction. This pathway can be summarized as shown in eq 5-8. On the other hand, it has been suggested that

$$RCO_2H + H_2SO_4 \rightleftarrows RCO_2H_2^+ + HSO_4^- \qquad (5)$$

$$RCO_2H_2^+ + H_2SO_4 \rightarrow RCO^+ + H_3O^+ + HSO_4^- \qquad (6)$$

$$RCO^+ + HN_3 \rightarrow RC(O)-N-\overset{+}{N}{\equiv}N: \rightarrow$$

$$RC(OH){=}N-\overset{+}{N}{\equiv}N: \rightarrow HO-\overset{+}{C}{=}N-R + N_2 \qquad (7)$$

(19) M. S. Newman and H. L. Gildenhorn, *J. Am. Chem. Soc.*, **70**, 317 (1948).
(20) L. P. Kuhn and A. H. Corwin, *J. Am. Chem. Soc.*, **70**, 3370 (1948).
(21) C. Schuerch, Jr., and E. H. Huntress, *J. Am. Chem. Soc.*, **71**, 2233 (1949).

$$\text{HO}\!-\!\overset{+}{\text{C}}\!=\!\text{N}\!-\!\text{R} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CO}_2 + \text{RNH}_3{}^+ \quad (8)$$

some form of the hydrazoic acid must attack an undehydrated form of the carboxylic acid. Several related pathways have been discussed,[3-5,7,8,14,16,21] and it is not useful at present to consider in detail the sequence and kinetics of events such as dehydration, rearrangement, and N_2 elimination from the HN_3 adduct. Rather, it can be observed simply that these mechanisms are thought to terminate with the same final step noted above (eq 8; the isocyanate has been isolated in a single case[22]) and that the participation of an "activated" form of HN_3 (e.g., nitrene) has been invoked on several occasions.[2,23,24]

The observation in the present work of two reaction phases having different kinetic characteristics and different carbon isotope effects indicates that two different pathways to the product must exist. The data available do not allow firm conclusions to be drawn—it is evident that this would require a great deal of additional experimental work going far beyond these investigations aimed at producing a reliable analytical technique—but aspects of the present observations can be interpreted as supporting both of the mechanisms mentioned above.

The first phase of the reaction can be tentatively associated with eq 5–8 on the following basis. First, comparison of trials B, C, D, and E indicates that k_I is independent of HN_3 concentration, a characteristic to be expected if eq 5 represents the rate-determining step. (The decrease in k_I observed in trial H can be attributed to a decrease in the rate of trapping of RCO^+ at very low concentrations of HN_3.) Second, the suppression of phase I by HSO_4^- (trial F) can be associated with a mass-law effect on eq 4 and 5, hindering acylium ion formation.[20] Although this pathway has been presented primarily in the context of aromatic acids, its relevance to aliphatic species like those investigated here has been supported[8] on the basis of observations regarding the H_2SO_4-catalyzed esterification of aliphatic acids.[25]

The second phase of the reaction appears to have at least one characteristic which has been associated with the second mechanism by previous investigators. Specifically, "activation" of the HN_3 participating in this reaction phase is indicated by the observations of trials A and E, in which preequilibration of the HN_3 with H_2SO_4 gave rise to the rapid initial production of CO_2 with an isotopic fractionation characteristic of phase II. When initiated in this way, however, the phase II pathway was apparently not sustained, since the ^{13}C content of the CO_2 soon dropped to levels characteristic of the much larger phase I isotope effect.

The fact that it is not enough simply to build a significant initial concentration of "activated" HN_3 in order to sustain phase II requires that some additional determining features be associated with phase II. In particular, catalysis by some phase II intermediate or product would be consistent with the observed competition between phases I and II, a phenomenon represented by the results of trial D, and with the decreased lag time noted in trial F. This catalysis could involve production of the "activated" HN_3 or any subsequent step of the reaction pathway. The k_{II} values observed in trials B, C, D, and

F are directly proportional to the corresponding initial HN_3 concentrations and, thus, do not support any second-order dependence on HN_3 concentrations, a feature which might be expected if, as suggested previously,[16] the activation of HN_3 involved more than single molecules.

Experimental Section

Apparatus. Schmidt decarboxylations were carried out in specially made, disposable, all-glass vessels having the shape of an inverted U and having, therefore, two compartments in which reactants could be isolated prior to mixing. The total internal volume of each vessel was $\sim$25 mL. Three tubes sealed to the arch linking the two compartments allowed the addition of samples and reagents and the recovery of CO_2. The $CHCl_3$–HN_3 reagent was stored in an all-glass apparatus which incorporated a calibrated delivery volume and which could be evacuated for degassing of the solution or pressurized for reagent delivery. The total volume of the storage vessel was $\sim$0.5 L.

Preparation of $CHCl_3$–HN_3 Reagent. The decarboxylating reagent solution was prepared and standardized as previously described.[13] The dried reagent was poured into the storage vessel together with $\sim$10 mL of 100% H_3PO_4. The reagent was thoroughly degassed by two repetitive freeze–thaw cycles in which the reagent was frozen at -131 °C (pentane slush[26]) and the head space above the frozen mass evacuated. Between freezings, the H_3PO_4 was thoroughly mixed with the $CHCl_3$–HN_3 reagent to facilitate removal of CO_2. Subsequently, the vessel was pressurized with nitrogen so that the reagent could flow from the vessel under closed conditions. In these circumstances, the reagent was stable at room temperature and lighting conditions for indefinite periods.

Preparation of Concentrated Sulfuric Acid Catalyst. In all cases Mallinckrodt concentrated sulfuric acid (analytical reagent, 95–98% H_2SO_4) was used as the catalytic phase. The $KHSO_4$–H_2SO_4 reagent was prepared by dissolving 0.3 g of $KHSO_4$ in 1 mL of the concentrated sulfuric acid.

Decarboxylation of Octanoic Acid. A known quantity of organic acid was injected into one side of the reaction vessel. The glass tube through which the sample had been added was sealed with a torch after 1.0 mL of H_2SO_4 had been added. In the same way, the reagent-side glass tube was sealed after 1.0 mL of the $CHCl_3$–HN_3 reagent had been delivered from the storage vessel.

The reaction vessel was cooled to -131 °C (pentane slush[26]), and the head space was evacuated after the solutions were thoroughly frozen. Subsequently, the pentane slush bath was replaced by a liquid nitrogen bath (-196 °C), and the break-seal sampling tube was sealed, under vacuum, with a torch. The vapor pressure of HN_3 is of sufficient magnitude to initiate an explosion if the break-seal tube is sealed with the mixture at -131 °C. Therefore, it is *imperative to seal the break-seal tube only after replacing the pentane slush with liquid nitrogen.*

The reactants were equilibrated at the reaction temperature (5 ± 2 °C obtained in a walk-in refrigerator), and the reaction vessel was tipped in order to allow the $CHCl_3$–HN_3 solution to drain from the reactant side into the sample compartment, initiating the reaction. The vessel was immediately attached to a vortex mixer for continuous, unattended stirring.

Reaction tubes were quenched by immersion in liquid nitrogen. The product CO_2 was removed by opening the break-seal under vacuum, thawing the reaction mixture, and distilling the CO_2 into a trap at -196 °C. The CO_2 was purified by repeated (3×) sublimation at -131 °C, and its isotopic composition was determined with a mass spectrometer system similar to that described by McKinney et al.[27]

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