THE JOURNAL OF Organic Chemistry®

Volume 26, Number 7 © Copyright 1961 by the American Chemical Society July 25, 1961

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

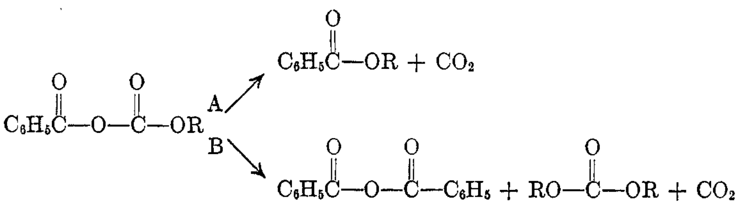
Aspects of the Mechanism of Decomposition of Mixed Carboxylic-Carbonic Anhydrides[1]

EDWARD J. LONGOSZ[2] AND D. STANLEY TARBELL

Received October 24, 1960

A kinetic study of the conversion of benzoic *n*-butylcarbonic anhydride to *n*-butyl benzoate (path A), and to benzoic anhydride and di-*n*-butyl carbonate (path B) has been made by measuring the rate of carbon dioxide evolution. The reaction, which shows erratic kinetics in the absence of added catalysts, is catalyzed by *N*-methylpiperidine, sodium methoxide, lithium fluoride, chloride and bromide, dry hydrogen chloride, dimethylaniline hydrochloride, and is not catalyzed by lithium perchlorate, benzoic acid, *n*-butyl benzoate, di-*n*-butyl carbonate, benzoyl peroxide, or tri-*n*-butylamine. The rate (in absence of added catalysts) is roughly the same in butylcarbitol, *n*-hexadecane and nitrobenzene, but is greatly accelerated in dimethylformamide. The proportions of products (paths A and B) are not altered by changes in solvent, temperature, or presence of catalysts. The results agree with the idea that the products are formed by a series of ionic chain reactions, which are initiated by the catalysts acting as nucleophiles. Optically active benzoic 2-octylcarbonic anhydride yields 2-octyl benzoate and dioctyl carbonate in refluxing pyridine with complete retention of configuration.

In an earlier paper,[3,4] it was shown that mixed carboxylic-carbonic anhydrides yield on heating two sets of products: the ester and carbon dioxide (path A), and the disproportionation products, the symmetrical anhydride, the dialkyl carbonate, and carbon dioxide (path B). A study of the effect of changes in structure of R on the proportions of A and B showed that path A is favored when the point of attachment of R is a secondary carbon, or a primary carbon with heavy substitution on the β-carbon. Both paths A and B occurred about equally when the alkyl group was primary, as in ethyl or butyl. Tertiary amines were found to increase the rate of formation, but not to alter the proportions, of products. Rearrangement of the mixed anhydride from (−)-2-octanol by heating at 150° without solvent proceeded with complete retention of configuration.[5]



$$C_6H_5\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OR \begin{cases} \xrightarrow{A} C_6H_5\overset{O}{\overset{\|}{C}}-OR + CO_2 \\ \xrightarrow{B} C_6H_5\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5 + RO-\overset{O}{\overset{\|}{C}}-OR + CO_2 \end{cases}$$

---

[1] A preliminary account of this work appeared in *Science*, **130**, 1425 (1959).

[2] National Science Foundation Predoctoral Fellow, 1958–1959.

[3] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959 .

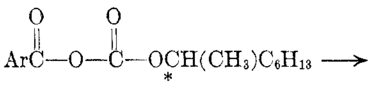
[4] (a) In a previous paper, dealing with the isolation of stable mixed anhydrides (D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958)) several references were missed, in addition to those cited, describing isolation of this type of structure: (b) E. Fischer and H. Strauss, *Ber.*, **47**, 317 (1914); (c) K. v. Auwers and E. Wolter, *Ber.*, **63**, 479 (1930); (d) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950); (e) D. B. Denney, *J. Am. Chem. Soc.*, **78**, 590 (1956).

[5] The possibility that a mixed anhydride with an optically active alkyl group might yield ester with retention of configuration of the alkyl group was suggested by F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4872 (1955), to explain some observations on formation of optically active alcohol from active methylphenylacetyl chloride and sodium peroxide. *Cf.* also P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1091 (1954).

The present paper describes some further sterochemical observations, and reports a kinetic study of the rearrangement of benzoic *n*-butylcarbonic anhydride. From the effects of many agents as catalysts, or noncatalysts, a fairly definite picture of the reaction mechanism emerges.

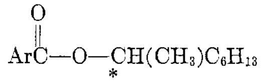
STEREOCHEMICAL STUDIES

The decomposition of the mixed anhydride by path A, where R is optically active, can be written with a formal similarity to the S_Ni reaction involving the chlorosulfite:



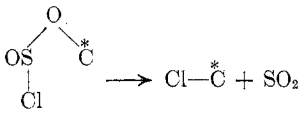
$$\mathrm{Ar}\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O\underset{*}{C}H(CH_3)C_6H_{13}\longrightarrow$$

I. Ar = C_6H_5
II. Ar = 2,4,6-$(CH_3)_3C_6H_2$



$$\mathrm{Ar}\overset{\overset{O}{\|}}{C}-O-\underset{*}{C}H(CH_3)C_6H_{13}$$

III. Ar = C_6H_5
IV. Ar = 2,4,6-$(CH_3)_3C_6H_2$



In some cases, thionyl chloride and an optically active alcohol in absence of pyridine lead to a chloride with retained configuration,[6] while a chloride of inverted configuration is formed in the presence of pyridine.[6] Later significant studies[7,8] have shown that the stereochemistry of the decomposition of chlorosulfites is dependent on the nature of the solvent; the whole range of results, from retention to inversion of configuration, can be obtained by varying the solvent.

We have therefore extended our previous observations,[3] and have found that, in refluxing pyridine, benzoic octylcarbonic anhydride (I) was rearranged to the ester (path A) and to dioctyl carbonate with complete retention of configuration, just as in the absence of pyridine. The corresponding mesitoic octylcarbonic anhydride (II) was also rearranged (without added solvent) to give octyl mesitoate (IV), with complete retention of configuration; the ester IV of the same rotation was prepared from optically active octyl alcohol and mesitoyl chloride. Thus, the stereochemistry of the reaction is unchanged by a change from no solvent to pyridine, and by an increase of hindrance around the carboxyl carbonyl group.

KINETIC STUDIES

The rate of rearrangement of benzoic *n*-butylcarbonic anhydride (V) was studied, following the reaction by measuring the rate of carbon dioxide evolution. Studies using dibutyl carbitol (dibutyl ether of diethylene glycol) as solvent at 155° showed that 70–75% of the theoretical amount of carbon dioxide was evolved, just as in the decomposition without solvent[3]; this corresponds to 40–50% of *n*-butyl benzoate (path A), with the remainder going to dibutyl carbonate and benzoic anhydride (path B).

The kinetic runs showed in some cases a first-order reaction, but the numerical values were not reproducible, varying from 2 to 13×10^{-4} sec.^{-1}, at 155.1°; most of the runs, however, did not yield linear first-order plots, but showed an increase in rate as the reaction proceeded, and also showed a lack of reproducibility from one run to another.

The possibility that these erratic results were due to systematic faults in equipment or technique was ruled out by measuring the rate of decomposition of benzyl chlorcarbonate in dibutyl carbitol at 155°:

$$C_6H_5CH_2OCOCl \longrightarrow C_6H_5CH_2Cl + CO_2$$

This reaction gave excellent first-order plots over the whole course of the reaction,[9] and its rate was unaffected by the presence of the reaction products.

The obvious explanation for the increase of rate during the reaction—that the products were catalyzing the reaction—was shown to be untenable, as far as the major products were concerned; addition of butyl benzoate, dibutyl carbonate, or benzoic anhydride to the mixed anhydride V in dibutyl carbitol did not affect the rate of decomposition of V. Nevertheless, there was no doubt about the autocatalytic effect of something present in the reaction mixture. This was demonstrated by using the reaction mixture from a completed kinetic run as the solvent for a second run; the rate for the second run was about ten times faster than the first run. Still a third experiment in the same reaction mixture gave a rate which was nearly twenty times the original rate. These observations were checked several times and although the amount of rate increase varied, an increase was always observed.

These observations suggested catalysis by trace impurities, which were produced in the reaction, and which might vary from one run to another in pure solvent, even though numerous procedures for washing the glass reaction flask and for washing the benzoic butylcarbonic anhydride were tried. There was no reaction between butyl carbonate and benzoic anhydride under the conditions of the kinetic runs.

---

[6] Summaries from the earlier literature are given by W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman, and A. D. Scott, *J. Chem. Soc.*, 1266 (1937).

[7] E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74,** 308 (1952); **75,** 3182 (1953).

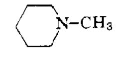
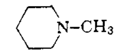
[8] D. J. Cram, *J. Am. Chem. Soc.*, **75,** 332 (1953).

[9] K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77,** 2774 (1955), reported good first order constants for this reaction in toluene and dioxane at 60–90°.

The effect of various possible catalysts on the rate of the reaction was investigated, with the results shown in Table I.

TABLE I

DECOMPOSITION OF BENZOIC-*n*-BUTYLCARBONIC ANHYDRIDE IN DIBUTYL CARBITOL; 155 ± 0.1°. EFFECT OF ADDITIVES ON RATE OF DECOMPOSITION

Additive	Solubility	Mole % of Additive	Relative Rate
None		—	1
$(n\text{-}C_4H_9)_3N$	+	8	1
$(n\text{-}C_4H_9)_3N$	+	90	1
	+	8	8
	+	19	12
$NaOCH_3$	−	5	15
 $(C_6H_5\text{—}\overset{O}{\overset{\|}{C}}\text{—}O)_2$	+	3	1[a]
$n\text{-}C_4H_9\text{—}OH$	+	30	1[a]
$C_6H_5\text{—}COOH$	+	4 to 12	1[b]
$C_6H_5\text{—}COONa$	−	5	Too fast to measure
$C_6H_5\text{—}N(CH_3)_2$	+	90	1
$C_6H_5\text{—}N(CH_3)_2.HCl$	−	1.4	20
Dry HCl	+	?	Too fast to measure
LiCl	−	2	Too fast to measure

[a] Solvent was butyl benzoate. [b] Solvent was also butyl benzoate and nitrobenzene.

The very strong catalytic effect of agents like sodium methoxide, lithium chloride, sodium benzoate, and dimethylaniline hydrochloride, which are apparently insoluble in dibutyl carbitol, is notable. Equally notable is the lack of catalytic activity of tri-*n*-butylamine, whereas the less sterically hindered *N*-methylpiperidine shows strong catalytic effects.

The first-order rate plots for the experiments using *N*-methylpiperidine and sodium methoxide are illustrated in Fig. 1. In these cases, the rate of decomposition steadily increased until approximately 50% reaction, then leveled off to follow a first-order rate law. The rate in the second half of the decomposition was at least two to three times the fastest rate observed in pure dibutyl carbitol, so it must be due to the presence of the bases. Moreover, a curve of this particular shape was never observed in pure solvent. Despite the fact that sodium methoxide was insoluble in the reaction medium, its influence seems to be similar to that of *N*-methylpiperidine.

Evidently, the catalytic action of the bases was greater than that of the by-products that caused rate increases in the determinations using pure dibutyl carbitol. A small interference from this source, however, can be seen from the slight curvature toward the completion of the reaction in experiments B and C.

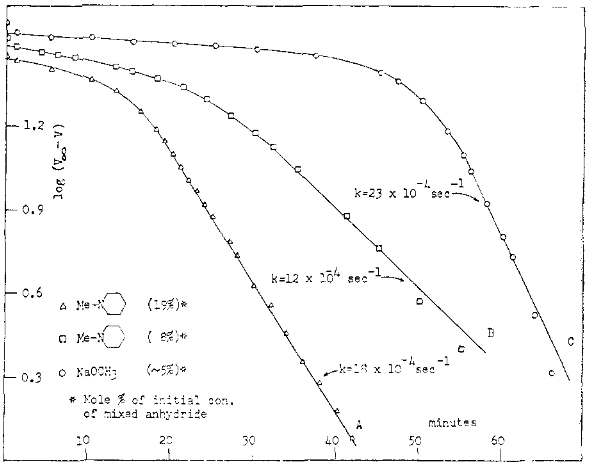


Fig. 1. Decomposition of benzoic-*n*-butylcarbonic anhydride in dibutyl carbitol; 155 ± 0.1°. Effect of bases. First-order rate plots

It was of interest to determine if the kinetic results of the very potent catalyst lithium chloride were similar to that of the basic substances. A measurable rate of decomposition of benzoic-*n*-butylcarbonic anhydride was observed at 115° in the presence of trace quantities of lithium chloride, and the first-order rate plots are illustrated in Figure II. In two experiments, the shape of the first-order plot was similar to that from the base catalyzed decompositions. With lithium chloride, however, the difference in rate between the initial and final stages of the decomposition was not as great. A run in the presence of lithium perchlorate was also made, but even though this salt was completely soluble in dibutyl carbitol, only a very small acceleration was observed.

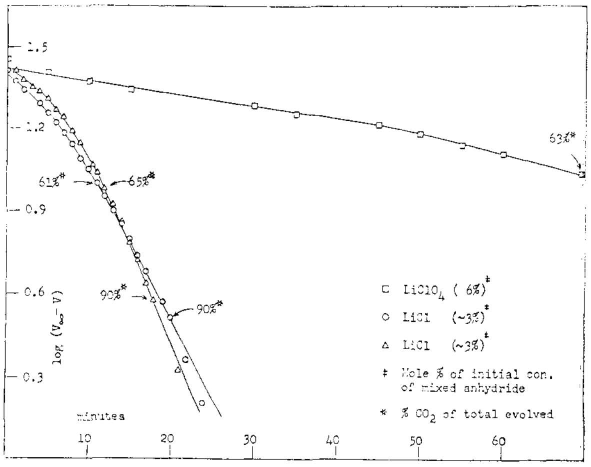


Fig. 2. Decomposition of benzoic-*n*-butylcarbonic anhydride in dibutyl carbitol; 115 ± 0.1°. Effect of lithium chloride. First-order rate plots

A series of rate measurements was also made in dibutyl carbitol containing a known quantity of hydrogen chloride. The shape of the first-order curves obtained from these decompositions at 115°

resembled the curves from the decomposition in pure solvent at 155°. A fairly linear portion was obtained from 10 to 50–70% carbon dioxide evolution, then the rate increased to approximately 100% its value in the linear portion. The rate of carbon dioxide evolution was roughly proportional to the hydrogen chloride concentration, although some erratic behavior was observed.

The effect of solvents of different polarity on the rate of a chemical process often establishes grounds for a possible reaction mechanism for that process. To this end, a measure of the rate of decomposition of benzoic-*n*-butylcarbonic anhydride at 155° was made in nitrobenzene, *n*-hexadecane, and *n*-butyl benzoate. In none of these solvents did the rate of decomposition depart greatly from the slowest rate measured in pure dibutyl carbitol. In fact, the rate of evolution of carbon dioxide from decomposition of the mixed anhydride in nitrobenzene and *n*-hexadecane was remarkably similar to that found in dibutyl carbitol. Although the evolution of carbon dioxide was faster when butyl benzoate was used as the solvent, the rate was still within the ranges found in dibutyl carbitol. The faster rate of decomposition in butyl benzoate may have been due to one of the factors causing the discrepancies in the measurements in pure dibutyl carbitol, or it may have been due to impurities indigenous to the solvent. A less thorough purification of the butyl benzoate was made compared to the other solvents used.

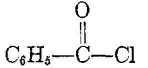
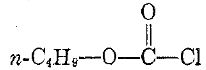
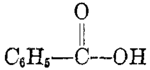
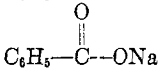
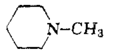
Although the dielectric constant of dimethylformamide (DMF) is similar to that of nitrobenzene, decomposition of benzoic-*n*-butylcarbonic anhydride in this solvent was accelerated to a great extent.[10] Whereas the rate of decomposition of the anhydride was too slow to be measurable in dibutyl carbitol at 97°, the decompositions in dimethylformamide at this temperature were complete in sixty to seventy minutes. The first-order plots of carbon dioxide evolution were not unlike the plots derived from reactions conducted in pure dibutyl carbitol at 155°.

The course of decomposition of the mixed anhydride in dimethylformamide was the same as the course of decomposition without solvent. The yield of carbon dioxide obtained was 75 ± 5%, indicating that approximately 50% of the anhydride decomposed to ester, and 50% to disproportionation products. This fact was verified by identity of the infrared absorption curve of the mixture freed of dimethylformamide with the mixture of products resulting from decomposition of the anhydride without solvent.

The greater solvating ability of dimethylformamide provided an opportunity to study the effect of ionic additives on the stability of the mixed anhydride. The salts listed in Table I, which were not soluble to any appreciable extent in dibutyl carbitol, were soluble in dimethylformamide, at least in the concentrations studied. The relative rates reported in Table II, using various soluble additives, afford a comparison of the times for 100% decomposition of benzoic-*n*-butylcarbonic anhydride. The rate accelerations observed were probably real, as measurement of the rate of decomposition in five separate experiments with no catalyst, showed fair agreement.

TABLE II

DECOMPOSITION OF BENZOIC-*n*-BUTYLCARBONIC ANHYDRIDE IN DIMETHYLFORMAMIDE; 97.5 ± 0.1°

Additive	Mole %	Relative Rate
None	—	1
LiCl	1.3	3
	2.7	3.5
	5.2	9
LiBr	3.9	3
LiF	3	2
$LiClO_4$	4.1	1
$(CH_3)_4NCl$	4.5	Too fast
 $C_6H_5-C(=O)-Cl$	3	1
 $n\text{-}C_4H_9-O-C(=O)-Cl$	3.7	1
 $C_6H_5-C(=O)-OH$	3	1
 $C_6H_5-C(=O)-ONa$	3	Too fast
	0.8	Too fast
	7.4	3

Lithium chloride, as well as lithium bromide, and, to a lesser degree, lithium fluoride acted as catalysts in the decomposition. As observed in the solvent dibutyl carbitol, lithium perchlorate again had no effect. Tetramethylammonium chloride was found to be a potent catalyst, but organic chlorine compounds such as benzoyl chloride and *n*-butyl chlorocarbonate were ineffective.

Whereas benzoic acid had no effect on the decomposition, its sodium salt was an extremely active catalyst. Even when less than 1 mole % of sodium benzoate was present, the evolution of carbon dioxide was too fast to measure; *N*-methylpiperidine had about the same effect as lithium chloride, but had to be present in five times the quantity of the latter to produce the same rate.

It is interesting to note that a first-order plot of carbon dioxide evolution in experiments where lithium chloride or *N*-methylpiperidine were used in dimethylformamide yielded curves similar to those obtained when these reagents were used in conjunction with dibutyl carbitol. The rate of

---

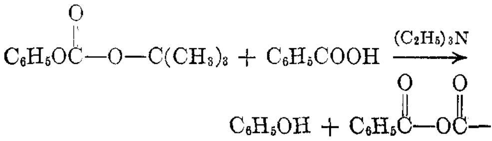
[10] The qualitative effect of dimethylformamide in accelerating displacement reactions at a saturated carbon is well known, and has been documented by quantitative measurements by H. E. Zaugg *et al.*, *J. Am. Chem. Soc.*, **82**, 2895, 2903 (1960).

evolution of carbon dioxide increased until approximately 50% reaction, when it leveled off to follow a first-order rate law.

Several decompositions were made in dimethylformamide using sodium benzoate or sodium acetate in small amounts. Because of the speed of the reaction, these measurements were made at 75°. The initial induction period was suppressed in two cases, although it still appeared in a third.

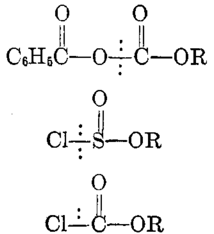
Several other qualitative observations may be mentioned. Benzoic benzylcarbonic anhydride was prepared, but it decomposed even at room temperature in the absence of added catalysts; the products could not be separated by distillation, but it was apparent from the infrared spectrum that decomposition had followed both paths A and B.

Benzoic 2-octylcarbonic anhydride appeared to decompose more slowly at 155° than the *n*-butyl compound. Decomposition of a crystalline sample of *p*-nitrobenzoic ethylcarbonic anhydride[4a] in dibutyl carbitol at 155° gave a rate ten times faster than the fastest rate observed for benzoic butylcarbonic anhydride. Recrystallization of this sample of mixed anhydride twice more, however, reduced the rate to one tenth of the former value; the first-order plot was curved in this case also. Apparently the *p*-nitrobenzoic mixed anhydride should be purified with great care before conclusions are drawn from its behavior.[11] Mesitoic 2-octylcarbonic anhydride failed to decompose at 155° at a measurable rate; attempts were made to prepare benzoic *t*-butylcarbonic anhydride from phenyl *t*-butylcarbonate,[12] benzoic acid, and triethylamine, but none of the desired product was obtained. Apparently the benzoate ion is too weak a nucleophile to bring about the desired reaction.



$$C_6H_5O\overset{O}{\overset{\|}{C}}—O—C(CH_3)_3 + C_6H_5COOH \xrightarrow{(C_2H_5)_3N} C_6H_5OH + C_6H_5\overset{O}{\overset{\|}{C}}—O\overset{O}{\overset{\|}{C}}—OC(CH_3)_3$$

Mechanism of mixed anhydride decomposition. The formal similarity, already mentioned, between the decomposition of the mixed anhydrides, the chlorosulfites and the chlorocarbonates is indicated below. Recent work[7–9] on the latter two types makes it clear that they split to ion pairs (Cl^-, ^+SOOR or Cl^-, ^+COOR) which then collapse with loss of sulfur dioxide or carbon dioxide, and the cleavage of the alkyl-oxygen bond. The stereochemical consequences when R is optically active depend on the nature of the solvent.



$$C_6H_5\overset{O}{\overset{\|}{C}}—O\,\vdots\,\overset{O}{\overset{\|}{C}}—OR$$

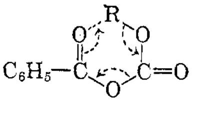
$$Cl\,\vdots\,\overset{O}{\overset{\|}{S}}—OR$$

$$Cl\,\vdots\,\overset{O}{\overset{\|}{C}}—OR$$

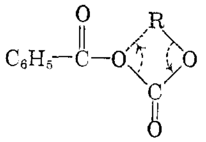
There is considerable evidence that this scheme does not obtain with the carboxylic carbonic anhydrides, except possibly in the case of the benzoic benzylcarbonic anhydride.[3,12a] The complete retention of configuration, even in the presence of pyridine, when R is optically active, the fact that the 2-octyl compound decomposes more slowly than the *n*-butyl compound, and that the neopentyl compound gives neopentyl benzoate without any evidence for skeletal rearrangement of the neopentyl group,[3] makes it unlikely that alkyl-oxygen cleavage does occur, with possible formation of a carbonium ion intermediate. The possibility of alkyl-oxygen cleavage is now being investigated by O^{18} studies.

The possibility that the decomposition of the mixed anhydrides is a free radical reaction is made unlikely by the fact that benzoyl peroxide does not act as a catalyst, and that the potent catalysts discovered in this study are all ionic compounds.

The mechanism for the decomposition of the mixed anhydride to ester, involving a cyclic transition state, cannot be ruled out on the basis of our stereochemical results, at least in the absence of pyridine. The two cyclic transition states VI and VII below, involve alkyl-oxygen cleavage and retention of configuration.



VI



VII

A transition state such as VI or VII does not explain the much greater tendency for the mixed anhydrides with heavy substitution on the β-carbon of the alkyl component to form ester. This result, however, can be justified on the basis that the heavy substitution inhibits the disproportionation reaction, thus allowing ester formation through VI or VII. The same may apply when the point of attachment is a secondary carbon atom.

---

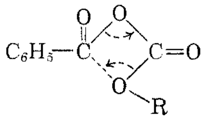
[11] *Cf.* T. B. Windholz, *J. Org. Chem.*, **23**, 2044 (1958).

[12] W. M. McLamore, S. Y. P'an, and A. Bavley, *J Org. Chem.*, **20**, 1379 (1955).

[12a] The very rapid rate of decomposition of the benzoic benzylcarbonic anhydride may be correlated with the observation that the mixed anhydrides, which may be intermediates in the ionic decomposition of phenylacetyl peroxides, cannot be isolated from bisphenylacetyl peroxide [P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950)] or from bis-*o*-iodophenylacetyl peroxide [J. E. Leffler and A. F. Wilson, *J. Org. Chem.*, **25**, 424 (1960)]. Decomposition of 4-methoxy-3′,5′-dinitrobenzoyl peroxide apparently gives the mixed anhydride $3,5\text{-}(O_2N)_2\text{-}C_6H_3COOCOOC_6H_4OCH_3$ (4) as an unstable intermediate, which forms the ester $3,5\text{-}(O_2N)_2C_6H_3COOC_6H_4OCH_3$ (4) [J. E. Leffler and C. C. Petropoulos, *J. Am. Chem. Soc.*, **79**, 3068 (1957)].

By increasing the polarization of the carboxylic carbonyl group, the tendency for the rearrangement to occur by the cyclic mechanism of VI might be expected to be increased. Indeed, when the mixed anhydride was made from a stronger acid, such as *p*-nitrobenzoic[11,13] or trifluoroacetic,[14] the reaction was reported to proceed predominantly to ester. Conversely, when the polarization of the carbonyl group is decreased, as it should be in the mesitoic carbonic anhydride, there should be a reduction in the tendency for ester formation. This seems to be the case with mesitoic ethylcarbonic anhydride, which underwent almost exclusive disproportionation. On the other hand, mesitoic-2-octylcarbonic anhydride exhibited almost exclusive ester formation, but again, this may be due to the constitution of the alkyl group in the carbonate portion of the mixed anhydride.

Another possible cyclic transition state for ester formation from a carboxylic-carbonic anhydride is that represented by structure VIII. This formulation involves acyl-oxygen cleavage in the carbonate portion of the mixed anhydride. This



type of transition state has been proposed in a similarly constituted system.[14]

The cyclic transition states VI, VII, and VIII, possible for the decomposition of a carboxylic carbonic anhydride, cannot be excluded for the mesitoate system on the grounds that the carbonyl group is sterically unavailable for reaction; many examples exist in which similarly hindered carbonyl groups do not react intermolecularly, but do so intramolecularly, with formation of five or six membered rings.[15]

The postulation of a mechanism involving a cyclic transition state for the formation of ester from a carboxylic-carbonic anhydride (path A) necessarily implies a different mechanism for the disproportionation reaction (path B), the formation of symmetrical anhydride and carbonate. It was shown that the specific mixtures of products obtained in the decomposition of the mixed anhydride were not determined by an equilibration process, as interconversion of the products did not occur under the conditions of the experiments. If the two processes under consideration (ester formation, path A; disproportionation, path B) occur by different mechanisms the ratio of path A to path B would be determined by the relative speed of the two paths. Alteration in the speed of one path relative to the other should be reflected in a change in the product ratios.

Decomposition of the mixed anhydrides in the presence of less than 5 mole % of tertiary amine, or lithium chloride, however, yielded practically the same product ratios as were obtained in the absence of these substances, although the reaction as a whole was accelerated to a marked degree. The temperature at which complete decomposition was usually attained within a short time in the presence of *N*-methylpiperidine was as much as 80° lower. Also, the temperatures at which decompositions were made in the presence of the amines differed by about 50°. In no case, however, was the ratio of products significantly changed.[16]

It is very unlikely that a substance accelerating the rate of one chemical process would accelerate the rate of a competing process to precisely the same degree. Yet, it would be necessary to draw this conclusion on the basis of two distinct mechanisms for the decomposition of the mixed anhydride, one for path A, and another for path B. Furthermore, decomposition of the mixed anhydride at widely different temperatures should be equivalent to altering the relative rates of the two paths, as it is unlikely, although possible, that two unrelated chemical processes have identical temperature coefficient.

If path A occurs by a unimolecular process, in which one molecule is involved in the rate determining step and path B occurs by a bimolecular process, in which two molecules are involved in the rate determining step, decomposing the mixed anhydride in solution should reduce the rate of path B to a much greater degree than the rate of path A. Hence, a decided increase in the yield of ester (path A) should be observed. However, when the mixed anhydride was decomposed in a 5% solution, by weight, in benzene or toluene, no alteration in product ratio was observed. In addition, the many decompositions of benzoic-*n*-butylcarbonic anhydride made under a variety of conditions, with and without catalysts for the purpose of kinetic measurements, never yielded more than 75 ± 5% carbon dioxide on the basis of the initial quantity of mixed anhydride. This indicates that the product ratio is immune to changes in concentration of anhydride and environment.

Our results indicate, therefore, that decomposition according to both paths A and B proceeds by a single rate-determining step. The results are best explained by the idea that decomposition of the mixed anhydride proceeds through a set of ionic

---

[13] A. Einhorn, *Ber.*, **42**, 2772 (1909).

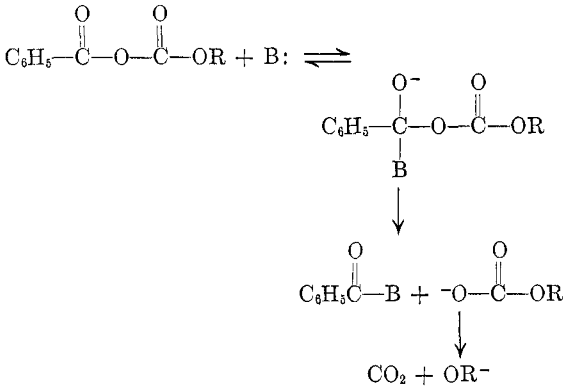
[14] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

[15] R. C. Fuson and Q. F. Soper, *J. Org. Chem.*, **9**, 193 (1944); R. C. Fuson, W. D. Emmons, and R. Tull, *J. Org. Chem.*, **16**, 648 (1951); R. C. Fuson and W. C. Hammann, *J. Am. Chem. Soc.*, **74**, 1626 (1952).

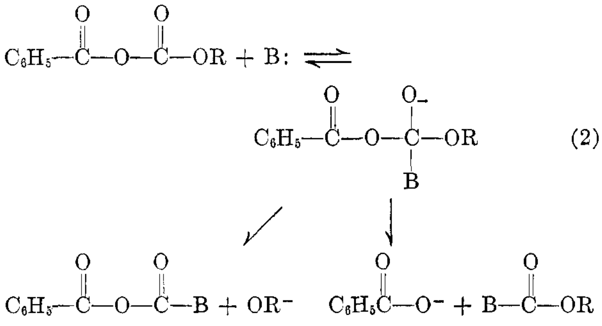
[16] In a paper which appeared after this paper was submitted, T. B. Windholz, [*J. Org. Chem.*, **25**, 1703 (1960)] reported that some mixed anhydrides form more ester at 200° than at 160°; high concentrations of boron trifluoride etherate favored ester formation. Windholz proposed a cyclic transition state analogous to VI for the ester formation.

chain reactions, of which some of the possibilities are indicated below.[17]

Representing a nucleophile, as B: which may be uncharged (a tertiary amine) or charged (a halide ion, for example), attack on the mixed anhydride may take place at the carboxyl carbonyl or the carbonate carbonyl.[18] In the former case, we can have the following, the charge on the structure in (1) depending of course on the charged or uncharged state of B:. Attack at the carbonate carbonyl can give:

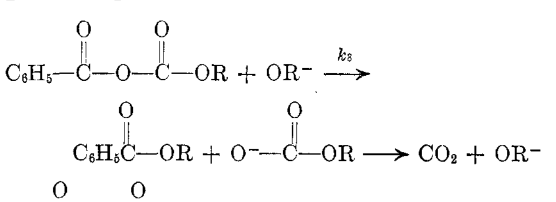


$$\begin{aligned}&C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR + B: \rightleftharpoons C_6H_5-\underset{B}{\overset{O^-}{C}}-O-\overset{\overset{O}{\|}}{C}-OR \quad (1)\\ &\longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}-B + {}^-O-\overset{\overset{O}{\|}}{C}-OR \longrightarrow CO_2 + OR^-\end{aligned}$$

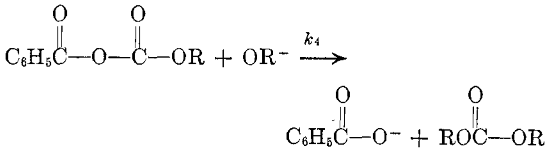


$$\begin{aligned}&C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR + B: \rightleftharpoons C_6H_5-\overset{\overset{O}{\|}}{C}-O-\underset{B}{\overset{O^-}{C}}-OR \quad (2)\\ &\swarrow\ C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-B + OR^- \qquad \downarrow\ C_6H_5\overset{\overset{O}{\|}}{C}-O^- + B-\overset{\overset{O}{\|}}{C}-OR\end{aligned}$$

The alkoxide ion OR^- generated according to (1) and (2) is the chain carrier, because it can attack at either carbonyl, as in (3) and (4), to generate products.

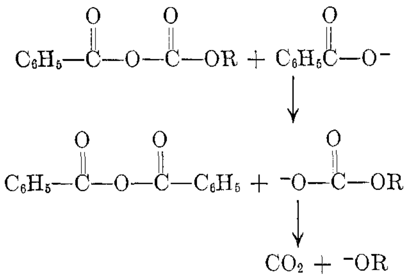


$$C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR + OR^- \xrightarrow{k_3} C_6H_5\overset{\overset{O}{\|}}{C}-OR + O^--\overset{\overset{O}{\|}}{C}-OR \longrightarrow CO_2 + OR^- \quad (3)$$



$$C_6H_5\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR + OR^- \xrightarrow{k_4} C_6H_5\overset{\overset{O}{\|}}{C}-O^- + RO\overset{\overset{O}{\|}}{C}-OR \quad (4)$$

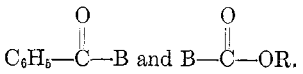
The $C_6H_5\overset{\overset{O}{/\!\!/}}{C}-O^-$, generated in (2) or (4), can attack unchanged anhydride at the carboxyl carbonyl:



$$\begin{aligned}&C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR + C_6H_5\overset{\overset{O}{\|}}{C}-O^-\\ &\downarrow\\ &C_6H_5-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-C_6H_5 + {}^-O-\overset{\overset{O}{\|}}{C}-OR \quad (5)\\ &\downarrow\\ &CO_2 + {}^-OR\end{aligned}$$

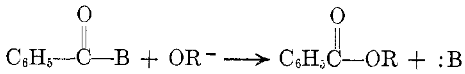
Attack of $C_6H_5-\overset{\overset{O}{\|}}{C}-O^-$ at the carbonate carbonyl gives no overall change. The formation of ester (path A) is due to reaction (3), and the disproportionation reaction (path B) is due to (4) followed by (5). Each benzoate ion produced in (4) can disappear only by (5), with the formation of an equal number of molecules of ROCOOR and $(C_6H_5CO)_2O$. The ratio of path A to path B products will be the ratio of the rates of attack of OR^- at the carboxyl carbonyl (reaction 3) to attack at the carbonate carbonyl (reaction 4) (*i.e.*, k_3/k_4). Since we observe experimentally that the A/B ratio is not affected by dilution, change in temperature or the nature of B:, it appears that the rate-determining stage of the decomposition is the attack of nucleophile B: according to (1) and (2). Presumably reactions (3) and (4) are very fast, and the temperature dependence of the ratio k_3/k_4 is close to unity.

The above discussion has neglected the reactions of products containing the catalyst B:, such as:

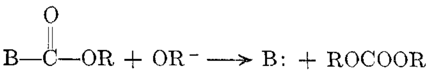


$$C_6H_5-\overset{\overset{O}{\|}}{C}-B \text{ and } B-\overset{\overset{O}{\|}}{C}-OR.$$

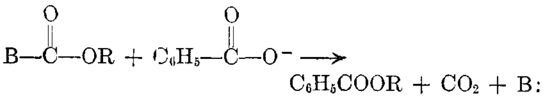
These may react with OR^- or $C_6H_5COO^-$ to regenerate B:, with the termination of a chain by using up the chain-carrying species.



$$C_6H_5-\overset{\overset{O}{\|}}{C}-B + OR^- \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}-OR + :B \quad (6)$$



$$B-\overset{\overset{O}{\|}}{C}-OR + OR^- \longrightarrow B: + ROCOOR \quad (7)$$



$$B-\overset{\overset{O}{\|}}{C}-OR + C_6H_5-\overset{\overset{O}{\|}}{C}-O^- \longrightarrow C_6H_5COOR + CO_2 + B: \quad (8)$$

In the supposedly uncatalyzed reaction, it is not certain whether there are traces of catalyst present, or whether there is a thermal cleavage of the anhydride to form ions which can initiate the chain reaction.

---

(17) Ionic chain reactions have been suggested in other cases by P. D. Bartlett and H. F. Herbrandson, *J. Am. Chem. Soc.*, **74**, 5971 (1952); *cf.* W. E. Bissinger, F. E. Kung, and C. W. Hamilton, *J. Am. Chem. Soc.*, **70**, 3940 (1948).

(18) Evidence supporting the existence of intermediates analogous to those below is given by V. Gold and E. G. Jefferson, *J. Chem. Soc.*, 1409, 1416 (1953), and by D. B. Denney and M. A. Greenbaum, *J. Am. Chem. Soc.*, **79**, 3701 (1957).

EXPERIMENTAL

Preparation of alkyl chlorocarbonates. All the chlorocarbonates used in this study were prepared by the action of phosgene on the respective alcohol. Details of the experimental procedure are described in a previous publication.[3]

Preparation of carboxylic-carbonic anhydrides. The carboxylic-carbonic anhydrides necessary in this study were synthesized from the respective carboxylic acid and alkyl chlorocarbonate. The method is described in detail in a previous publication.[3]

Rearrangement of optically active benzoic 2-octylcarbonic anhydride in pyridine. The mixed anhydride was generated in the usual way using 2-octyl chlorocarbonate generated from 2-octanol having b.p. 75° (4 mm.), n_D^{25} 1.4235, α_D^{25} + 6.19 ± 0.02° (neat, l = 1). The optically active benzoic 2-octylcarbonic anhydride (8.0 g., 0.029 mole) was placed in a 50-ml. round bottomed flask containing 20 ml. of pyridine, which had been purified by distillation from barium oxide. The mixture was heated at reflux (113°), during which time the color of the solution progressively changed from pink to red to brown. After 8 hr. of heating, the mixture was cooled, taken up in ether, and washed with water, dilute hydrochloric acid, saturated sodium bicarbonate solution, and water. After drying the ether solution over anhydrous sodium sulfate, the ether was removed at reduced pressure, leaving behind a dark brown oil. Distillation of this material yielded 1 g. of almost pure 2-octanol with α_D^{25} + 6.52 ± 0.01°, and 3.5 g. of a mixture of 2-octyl benzoate and di-2-octyl carbonate, b.p. 122–129° (1 mm.), n_D^{25} 1.4628–1.4753. The reported[19] b.p. for 2-octyl benzoate is 171° (20 mm.), n_D^{25} 1.4840. An authentic sample had b.p. 113–116° (0.5 mm.), n_D^{20} 1.4885. The reported[20] b.p. for di-2-octyl carbonate is 168° (13 mm.); an authentic sample had b.p. 118–123° (0.7–1 mm.), n_D^{25} 1.4280. The dark brown residue from the distillation yielded 1.5 g. of benzoic anhydride upon recrystallization.

Saponification of the mixture of 2-octyl benzoate and carbonate with alcoholic potassium hydroxide yielded 2-octanol with b.p. 72–73° (8 mm.) n_D^{25} 1.4232, α_D^{25} + 6.17 ± 0.01° (neat, l = 1).

Preparation of optically active 2-octyl mesitoate from mesitoyl chloride and (+)-2-octanol. Mesitoyl chloride (4.2 g., 0.023 mole) and 2-octanol (3.0 g., 0.023 mole) with α_D^{25} + 6.19 ± 0.02° (neat, l = 1) were placed in a 25 ml., round bottomed flask containing 15 ml. of dry pyridine. After heating the mixture on a steam-bath for 2 hr., it was cooled, taken up in ether and washed successively with water, dilute hydrochloric acid, dilute sodium hydroxide, and water. After drying the ether solution, the solvent was removed under reduced pressure and the nonvolatile oil purified by fractionation through a vacuum-jacketed Vigreux column (100 × 10 mm.). There was obtained 3.93 g. (62%) of 2-octyl mesitoate having b.p. 139–140° (0.5 mm.), $n_D^{24.5}$ 1.4869, α_D^{25} + 24.03 ± 0.02° (neat, l = 1). This corresponded with the properties previously reported[3] for an authentic sample of 2-octyl mesitoate.

Rearrangement of optically active mesitoic-2-octylcarbonic anhydride. The mixed anhydride was generated from mesitoic acid and the chlorocarbonate of 2-octanol; the 2-octanol had α_D^{25} + 6.19 ± 0.02° (neat, l = 1). The rearrangement was carried out in the usual way, and yielded mainly 2-octyl mesitoate. The last, and most pure fraction had b.p. 153–154° (1.5 mm.) $n_D^{24.5}$ 1.4869, α_D^{25} + 24.01 ± 0.02° (neat, l = 1).

Rearrangement of benzoic benzylcarbonic anhydride. When prepared in the usual manner, this anhydride decomposed with evolution of carbon dioxide at room temperature, and heating to 50° hastened this decomposition. Distillation of the rearrangement product yielded fractions boiling between 120–140° (0.2 mm.), n_D^{25} 1.5615 to 1.5641. The b.p. for benzyl benzoate[21] is 185° (15 mm.) n_D^{21} 1.5681; dibenzyl carbonate,[22] b.p. 203° (12 mm.); benzoic anhydride,[23] b.p. 360°, n_D^{15} 1.5767. The infrared absorption curve of the distillate showed the presence of all three products in all fractions, with benzyl benzoate concentrated in the lower boiling fractions, and dibenzyl carbonate and benzoic anhydride concentrated in the higher boiling fractions.

Preparation of phenyl-t-butyl carbonate. This mixed carbonate was prepared from *t*-butyl alcohol and phenyl chlorocarbonate following the method of McLamore.[12] It was not purified by distillation, as the infrared absorption spectrum of this carbonate had a strong peak at 5.69 μ, but no others in this region.

Attempted preparation of benzoic-t-butylcarbonic anhydride. Phenyl-*t*-butyl carbonate (3.55 g., 0.0183 mole), 15 ml. of ether, and 0.5 ml. of triethylamine were placed in a 50 ml. flask. Benzoic acid (2.23 g., 0.0183 mole) in 10 ml. of ether was slowly added to this mixture. After heating the solution at the boiling point of ether for 1 day, it was obvious from the infrared absorption curve of a sample of the mixture, that no chemical change had taken place. Stripping the mixture of ether and heating it to 75° in the presence of *N*-methylpiperidine likewise produced no change.

Purification of solvents used in kinetic measurements. A. *Dibutyl carbitol* was purchased from Carbide and Carbon Chemicals Co. It was vigorously shaken with water to extract alcoholic impurities, all of which were soluble in water. It was then dried over Drierite, and fractionally distilled from sodium under reduced pressure through a Vigreux column (15 × 1 in.). The main fraction boiled at 110–110.5° (5 mm.), n_D^{25} 1.4210. The reported[24] index of refraction is n_D^{20} 1.4241.

B. *n-Hexadecane* was Eastman Kodak practical grade. Approximately 500 g. of *n*-hexadecane with 80 ml. of concd. sulfuric acid was heated on a steam bath with vigorous stirring. When the sulfuric acid turned dark, it was replaced with fresh acid. This treatment was continued until the acid remained colorless, and required approximately eight changes. The hexadecane was washed thoroughly with water, a saturated solution of sodium bicarbonate and more water, then dried over sodium sulfate. Fractional distillation under reduced pressure through a Vigreux column (25 × 2 cm.) yielded constant boiling material with b.p. 114–115° (1.5 mm.), n_D^{26} 1.4320.

C. *Nitrobenzene* was Eastman Kodak white label grade. It was further purified by treatment with phosphorus pentoxide, then fractionally distilled under reduced pressure. The constant boiling material had b.p. 80° (7 mm.).

D. *n-Butyl benzoate* was Eastman Kodak white label grade. It was purified by drying over Drierite, then fractionally distilling under reduced pressure. This material had b.p. 113° (6 mm.).

E. *N,N-Dimethylformamide* was purified by the method of Thomas and Rochow,[25] which involved thorough drying over Drierite, vigorous shaking with barium oxide, and fractional distillation under reduced pressure. The material obtained by this treatment was neutral and had b.p. 64° (31 mm.).

Kinetic measurements of the decomposition of benzoic-carbonic anhydrides. The reaction vessel used for the kinetic measurements was a 50-ml. Erlenmeyer flask, fitted with a standard taper joint for attachment to an Allihn Condenser (12 × 1 in.) and a stopcock (4 mm. bore) for gaining entry to

---

(19) A. J. H. Houssa and H. Phillips, *J. Chem. Soc.*, 2510 (1929).

(20) H. Hunter, *J. Chem. Soc.*, 1389 (1924).

(21) C. A. Kohn and W. Trantom, *J. Chem. Soc.*, **75**, 1155 (1899).

(22) C. A. Bischoff, *Ber.*, **36**, 159 (1903).

(23) A. Kaufmann and A. Luterbacher, *Ber.*, **42**, 3483 (1909).

(24) J. Kooi, *Rec. Trav. Chim.*, **74**, 137 (1955).

(25) A. B. Thomas and E. G. Rochow, *J. Am. Chem. Soc.*, **79**, 1843 (1957).

the flask. The top of the condenser was attached to a gas buret through a three-way stopcock by means of flexible rubber tubing. All stopcocks and joints were lubricated with Dow-Corning silicone grease. The system was often checked for leaks by pressuring it with carbon dioxide, but always found to be satisfactory.

The reaction vessel was constantly agitated during the course of a kinetic experiment by a shaking device attached to the reaction flask.

The constant temperature bath consisted of a stainless steel beaker (9 × 6.5 in.), filled with Fisher bath wax, and inserted into a metal can (12 × 9 in.), with the space between the vessels packed with insulating material. The wax was heated to within 10–20° of the desired temperature by means of a 750 watt immersion heater. Final temperature control was maintained by means of a vapor pressure type thermostat, attached to a 125-watt knife blade heater through a relay. The shaking motion of the reaction flask in the wax bath was sufficient to provide adequate circulation, since temperature control to within 0.2° could generally be maintained during an experiment.

A kinetic measurement was preceded by cleaning of the reaction flask. At the beginning stages of the work, sulfuric acid–dichromate was used, but it was found that hot caustic was equivalent to the acid wash as far as the effect on the rates was concerned. In either case, the flask was repeatedly rinsed with distilled water and acetone, and dried overnight at 120°. Glass wool was placed in the reaction flask and the latter inserted into the constant temperature bath and attached to the condenser. The entire apparatus was flushed with carbon dioxide, which was dried by passing it through Drierite. The solvent to be used in the experiment was thoroughly saturated with carbon dioxide at room temperature, then injected into the reaction flask by means of a syringe. The shaker was started, and the system equilibrated for approximately 1 hr. In order to start a kinetic measurement, a weighed sample of the carboxylic-carbonic anhydride was injected into the solvent in the reaction flask through the stopcock, the opening of which was protected from the atmosphere by a rubber diaphragm. After the addition of sample, which generally took less than 30 sec., the shaker was started, and readings of carbon dioxide evolution were taken at appropriate time intervals, depending on the speed of the particular decomposition. A shield surrounding the gas buret was effective in keeping its temperature fairly constant. The decomposition was allowed to continue until a constant volume of gas was evolved, and this was taken as V_∞. Each volume was corrected to volume at STP and a plot of $\log (V_\infty - V)$ versus time was made.

In the catalyzed decompositions, the catalyst was added to the solvent before the latter was saturated with carbon dioxide, or if insoluble, it was placed in the reaction flask.

When hydrogen chloride was used as catalyst, a small quantity was bubbled into dibutyl carbitol, and its concentration determined by titration with standard sodium hydroxide, using 95% ethanol as solvent. The end-point was determined with a *p*H meter. Solutions with a desired concentration of hydrogen chloride were made up by dilution of this stock solution with pure dibutyl carbitol, and the concentrations were always checked by titration.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

Trifluoroacetonitrile Addition Reactions. I. Ethylene

G. J. JANZ AND J. J. STRATTA

Received February 24, 1960

It is shown that trifluoroacetonitrile reacts readily with ethylene in the homogeneous gas phase at moderately high temperatures (300°–500°) with the formation of 4,4,4-trifluorobutyronitrile when the reactants are mixed in equimolar ratio at atmospheric pressure. Some evidence for the formation of another product, most likely 4,4,4-trifluorocapronitrile in smaller amounts is reported. Equilibrium yields of 4,4,4-trifluorobutyronitrile as predicted from thermodynamics are apparently readily attained at 400°, *i.e.* thermodynamic control can be achieved.

In the preceding communications in this series the reactions of simple dienes with trifluoroacetonitrile have been described. The nitrile group exhibited dienophilic properties with the facile formation of 2-trifluomethyl-substituted pyridines at atmospheric pressure and moderately high temperatures (350°–520°). The present paper is the first in a series describing the results of similar studies of the reactions of simple olefins and acetylenes with trifluoroacetonitrile in this laboratory. The thermal addition of trifluoroacetonitrile to ethylene, and the thermodynamics of the process are reported.

EXPERIMENTAL

Chemicals. The trifluoroacetonitrile (b.p. −68°) was a commercial sample (Columbia Organic Chemicals) of minimum 95% purity. The ethylene (b.p. −104°) was a commercial C.P. grade sample (Matheson Co.). Portions of both chemicals were repeatedly redistilled by vacuum transfer techniques to remove dissolved air and other noncondensable gases before use in the experiments.

Apparatus and procedure. A static system was used, since an interest was to explore the thermal stabilities of the reactants, and the possibility of thermodynamic control for the addition reaction. Vacuum transfer techniques were used in an all glass system as illustrated in Fig. 1. Predetermined amounts of the reactants (sufficient to give a pressure of about 1 atm. initially at the reaction temperature) were transferred from the ampoules (B) to the storage trap (A). The 5-l. reaction vessel (J) was attached in place of one of the ampoules by its side arm to the manifold, evacuated, filled with the reactants from the trap, and sealed off with a torch after the reaction charge had been frozen (−195°) into the small finger type trap. The flask J was then positioned in the furnace and resealed to the vacuum manifold as shown in Fig. 1. The reaction temperature was monitored by two chromel-alumel thermocouples. On completion of an experiment the contents of the flask J were transferred to a cold trap E (−195°) and J was removed from the system. The nature of the product mixture in E was investigated by the conventional techniques as described below.

---

(1) G. J. Janz and M. A. De Crescente, *J. Org. Chem.* **23**, 765 (1958); J. M. S. Jarvie, W. E. Fitzgerald, and G. J. Janz, *J. Am. Chem. Soc.* **78**, 978 (1956).