

Registry No.—3a, 40329-00-8; 3b, 40329-01-9; 4, 40329-02-0; 4 disilver salt, 40329-03-1; *o*-iodophenylphosphorus oxychloride, 40329-04-2; *o*-iodophenol, 533-58-4; phosphorus oxychloride, 10025-87-3; *o*-iodophenylphosphoric acid 40329-05-3; disilver salt of *o*-iodophenylphosphoric acid, 40329-06-4; silver nitrate, 7761-88-8; *o*-iodosodichloridophenoxyporphorous oxychloride, 40329-07-5; chlorine, 7782-50-5.

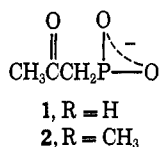
Thermal Decomposition of a β -Ketophosphonic Acid¹

RONALD KLUGER

Searle Chemical Laboratory, Department of Chemistry,
University of Chicago, Chicago, Illinois 60637

Received January 22, 1973

The decarboxylation of β -ketocarboxylic acids is a well-known reaction of synthetic² and mechanistic³ interest. The reaction has received considerable kinetic study⁴ and studies on its solvent dependence suggest that the reaction proceeds *via* an internally hydrogen-bonded transition state.⁵ It has been proposed that β -ketosulfonamides, generated *in situ* by oxidation of 3-hydroxysulfoamides, decompose in an analogous fashion, although the intermediate keto compound has not been isolated.⁶ A decomposition reaction of β -ketophosphonic acids by a similar route would be expected to lead to the initial production of the postulated (but never observed) species, monomeric metaphosphate,⁷ and residual ketone. In neutral aqueous solution at room temperature, spontaneous decomposition of protonated β -ketophosphonic acids is not observed,⁸ whereas protonated β -ketocarboxylic acids are readily decarboxylated.⁴ We have examined the thermal lability of the monosodium salt of acetylphosphonic acid (1) and of its methyl ester (2) in



order to determine if conversion to metaphosphate and ketone (eq 1) can be brought about if more extreme conditions than those required for the analogous decarboxylation reaction are employed.

(1) Support of this work by the Research Corporation is gratefully acknowledged.

(2) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1961, pp 446-448.

(3) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, pp 116-120.

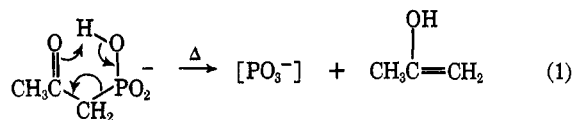
(4) K. J. Pedersen, *J. Amer. Chem. Soc.*, **51**, 2098 (1929), and references cited therein.

(5) F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).

(6) E. J. Corey and T. Durst, *ibid.*, **88**, 5656 (1966).

(7) W. W. Butcher and F. H. Westheimer, [*J. Amer. Chem. Soc.*, **77**, 2420 (1955)] invoked this species to explain the peculiar pH dependence of the rate of hydrolysis of methyl phosphate, noting that Todd proposed in a lecture in 1954 that metaphosphate was an intermediate in phosphorylation reactions. The current status and applications of the metaphosphate hypothesis have recently been summarized by D. G. Gorenstein [*J. Amer. Chem. Soc.*, **94**, 2523 (1972)].

(8) R. Kluger and P. Wasserstein, *ibid.*, **95**, 1071 (1973).



Experimental Section

The dimethyl ester of acetylphosphonate can be conveniently prepared by published procedures.^{8,9,10} Dimethyl acetylphosphonate was converted to the monosodium salt of methyl acetylphosphonate (2) by refluxing in acetone with a twofold excess of sodium iodide. The white precipitate was isolated by filtration and was recrystallized from ethanol to which ether was added, needles, mp 181-182°. *Anal.* Calcd for C₄H₅O₄PNa: C, 27.60; H, 4.63; P, 17.79. Found: C, 27.62; H, 4.64; P, 17.95. The sodium salt of acetylphosphonic acid (1) was prepared as reported from the monomethyl ester.⁸

Studies of the thermal decomposition of these compounds were performed utilizing a bulb-to-bulb distillation apparatus under high vacuum, in order to permit the quantitative isolation of products. Acetylphosphonic acid monosodium salt (0.30 g) was placed in one arm of the apparatus and, after pressure was below 0.1 Torr, heat was applied with an oil bath; the other arm of the apparatus was cooled in liquid nitrogen. Decomposition of the compound occurs at its melting point (146°) and heating to 150° was required to affect complete conversion. The material in the liquid nitrogen cooled arm was readily identified by its physical properties as being acetone; the isolated yield of acetone was 0.11 g (90%). The residue in the heated arm (0.18 g) was a high-melting white powder whose infrared spectrum was identical with that reported by Corbridge and Lowe¹¹ for (NaPO₃)_n, polymetaphosphate glass. Heating the sodium salt of the monomethyl ester of acetylphosphonate to 185° (above its melting point) did not lead to the salt's decomposition.

Discussion

The reaction proposed in eq 1 (or its intermolecular counterpart) appears to be operative under the conditions studied (150°, no solvent) for 1. The monomethyl ester of the phosphonate 2 is stable under conditions which lead to the immediate decomposition of the parent salt. Therefore, the availability of the proton of the phosphonic acid appears to be a requirement for the decomposition reaction; methyl transfer does not occur. This conforms with (but does not necessarily require) the mechanism in eq 1. The fact that the polymer of metaphosphate (rather than the elusive monomer or a lower oligomer¹²) is isolated is presumably a result of the reactive monomeric anion being produced under the conditions of high temperature necessary for the decomposition.

The thermal decomposition reaction of β -ketophosphonates is potentially of synthetic utility where the stability of the phosphonate relative to a carboxylate may be of value in an acetoacetic ester type synthesis.¹³ The enolate of the phosphonate diester is a well-studied species⁹ which should be readily alkylated.^{13a} Ketones containing an α -halo substituent can be converted to β -ketophosphonate compounds by the Arbusov or related reactions¹⁴ involving addition of a

(9) F. A. Cotton and R. A. Schunn, *ibid.*, **85**, 2394 (1963).

(10) H. I. Jacobson, M. J. Griffith, S. Preis, and E. V. Jensen, *ibid.*, **79**, 2608 (1957).

(11) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, 493 (1954).

(12) E. Thilo, *Angew. Chem., Int. Ed. Engl.*, **4**, 1061 (1965).

(13) C. R. Hauser and B. E. Hudson, Jr., *Org. React.*, **1**, 266 (1942).

(13a) NOTE ADDED IN PROOF.—P. A. Grieco and C. S. Pogonowski [*J. Amer. Chem. Soc.*, **95**, 3071 (1973)] have recently developed methods for alkylation of the 4 position of dimethyl acetylphosphonate.

(14) G. M. Kosolapoff, *Org. React.*, **6**, 273 (1951).

phosphite to a "positive carbon atom" adjacent to the carbonyl function. Carboxylation reactions generally require proceeding *via* the α -keto carbanion. The differences in polarity of precursor species to the phosphonate and carboxylate, respectively, should be of utility for specific synthetic strategies.

Registry No.—1, 40463-76-1; 2, 40463-77-2; dimethyl acetonylphosphonate, 4202-14-6; sodium iodide, 7681-82-5.

**Induced Decomposition of
Di-*tert*-butyl Peroxide Using
Chlorotris(triphenylphosphine)rhodium(I)/
Hydrogen**

L. KIM* AND K. C. DEWHIRST

*Shell Development Company,
P. O. Box 481, Houston, Texas 77001*

Received March 2, 1973

Heterogeneous hydrogenation of peroxides using various metal systems is well known.¹ The fact that nearly quantitative yields of alcohols are obtained without apparent secondary radical reactions such as β scission suggest either concerted cis addition of hydrogen or a very rapid sequential reaction which does not allow the escape of free alkoxy radicals. We now wish to report the induced decomposition of di-*tert*-butyl peroxide in a chlorotris(triphenylphosphine)rhodium(I)/hydrogen homogeneous system.

Hydrogenation of di-*tert*-butyl peroxide using chlorotris(triphenylphosphine)rhodium(I) in benzene solution yielded *tert*-butyl alcohol and acetone. The reaction is first order in catalyst, first order in peroxide (Figure 1), zero order in hydrogen pressure, and inversely proportional to added triphenylphosphine above a 1:1 weight ratio based on catalyst. It can be seen in Table I that only simple phosphine-rhodium (or ruthenium) halide systems are effective. Uncatalyzed reactions

TABLE I
EFFECT OF VARIOUS CATALYST SYSTEMS ON
SELECTIVITY TO *tert*-BUTYL ALCOHOL^a

Registry no.	Catalyst ^b	% reacted di- <i>tert</i> -butyl peroxide (conversion)	Yield <i>tert</i> -butyl alcohol based on reacted peroxide ^c (selectivity)
14694-95-2	L ₃ RhCl	29	58
14973-89-8	L ₃ RhBr	53	59
18284-36-1	L ₄ RhH	2	
13938-94-8	L ₂ (CO)RhCl	1	
20097-11-4	L ₂ (NO)RhCl ₂	1	
15529-49-4	L ₃ RuCl ₂	23	61

^a Data for 0.043 mmol of catalyst, 20 mg of Ph₃P, 5.4 mmol of di-*tert*-butyl peroxide, 30 ml of benzene, 600 psig of hydrogen, 120°, and 1 hr reaction time. ^b L = triphenylphosphine. ^c Remainder was converted to acetone.

(1) For discussion and references see P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, p 489.

under identical conditions (but no catalyst or catalyst but no hydrogen) show only trace (1–3%) peroxide decomposition. Introduction of either radical-stabilizing solvents or effective hydrogen-transfer agents resulted in increased selectivity to *tert*-butyl alcohol (Table II).

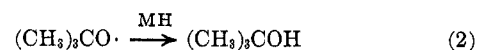
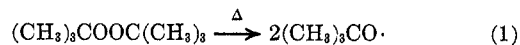
TABLE II
EFFECT OF VARIOUS ADDITIVES ON
SELECTIVITY TO *tert*-BUTYL ALCOHOL^a

Additive	g	% reacted di- <i>tert</i> -butyl peroxide (conversion)	Yield <i>tert</i> -butyl alcohol based on reacted peroxide ^b (selectivity)
Tetralin	1.0	80	94
Phenol	1.0	9	100
<i>m</i> -Cresol	0.5	85	99
Ionol ^c	0.5	57	86

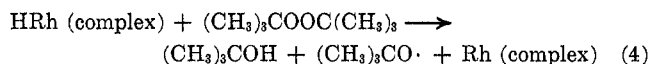
^a Data for 0.043 mmol of (Ph₃P)₃RhCl, 20 mg of Ph₃P, 5.4 mmol of di-*tert*-butyl peroxide, 30 ml of benzene, 600 psig of hydrogen, 120°, and 1 hr reaction time. ^b Remainder converted to acetone. ^c 2,6-Di-*tert*-butyl-4-methylphenol.

Of the additives tested, *m*-cresol appeared to be the best from the standpoint of reaction rate and selectivity. Quantitative measurements indicate that *m*-cresol was not destroyed in the reaction.

A mechanism which involves no induced decomposition and only simple abstraction of rhodium hydrogen seems unlikely because (1) the rate of peroxide decom-



position is rapid relative to identical metal-free systems and (2) the rate of disappearance of peroxide is proportional to catalyst concentration, while the selectivity to *tert*-butyl alcohol is independent of catalyst



concentration. We suggest that a rhodium-hydrogen complex leads to the induced decomposition of peroxide resulting in the formation of free radicals. It should be noted that not all of the rhodium complexes in Table I induce peroxide decomposition. This might be explained by analogy to olefin hydrogenation activity in which these complexes exhibit diverse activity.² The inverse dependence on triphenylphosphine might be explained by loss of a triphenylphosphine moiety in the course of reaction; the facility with which the various complexes in Table I could lose a triphenylphosphine moiety is in general agreement with the observed induced decompositions.² Indeed, induced decomposition of nonmetallic systems is well known. Induced decomposition of di-*tert*-butyl peroxide has been reported by workers at Shell³ in explaining increased decomposition rates of neat di-*tert*-butyl peroxide and by

(2) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 263 (1972), and references cited therein.

(3) E. R. Bell, F. F. Rust, and W. E. Vaghan, *J. Amer. Chem. Soc.*, **72**, 337 (1950).