Thermal and Photochemical Decomposition of Ethyl and Isopropyl Pyruvate in the Vapor Phase[1]

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The decomposition of ethyl and isopropyl pyruvate in the vapor phase has been effected by thermal and photochemical means. In the thermal decomposition a variety of products are formed, the relative and absolute yields of which are functions of reaction time and temperature. Noticeably conspicuous is the very low yield of the simple ester (*i.e.*, ethyl acetate from ethyl pyruvate) which is contrary to the implication of an earlier worker. The photochemical decomposition yields fewer products, among which are those formed in solution (benzene) from the same esters. Modest pressures of oxygen do not significantly affect the efficiency of the photodecomposition. Both the pyrolysis and photolysis apparently involve complex radical fragmentation.

The purpose of the present investigation originally was to attempt to correlate the photolytic behavior of the pyruvate esters in the vapor phase with that observed in solution.[2,3] During the course of the work it became apparent that data on the thermal decomposition of these compounds would be of great value in interpreting the photochemical results. Thermal decarbonylation, catalyzed by powdered iron and ground glass, has been employed as a synthetic route to 2-carbethoxycyclohexanone from the corresponding α-keto ester obtained from condensation of ethyl oxalate with cyclohexanone.[4] This appears to be somewhat a special case however, since the nature of the catalyst or catalysts is not understood. Two widely used textbooks[5,6] state, based on the work of Calvin and Lemmon in 1947,[7] that ethyl pyruvate thermally decomposes at 130° to yield carbon monoxide and ethyl acetate (products analogous to those obtained in ref. 4) as the principal products. Labeling experiments showed that it was the carboxyl carbonyl that was eliminated. Since Calvin's paper was only a brief communication, no experimental conditions other than the temperature were given. In this paper it was not stated whether the reaction was or was not catalyzed, but in ref. 5 and 6 the clear implication is that the reaction proceeds under the given conditions without catalysis.

We wish now to report totally different observations with regard to the products formed and reaction temperature necessary for noncatalyzed thermal decomposition of ethyl pyruvate (and the results of similar studies on the isopropyl ester), as well as the results of photochemical studies on the two esters in the vapor phase. The solution-phase photochemistry of several α-keto esters has been studied recently by several investigators.[2,3,8] In alcoholic solvents at room temperature, both ethyl pyruvate and ethyl benzoylformate are efficiently photoreduced to the corresponding pinacols.[3,8] At elevated temperature ethyl benzoylformate undergoes intramolecular hydrogen abstraction yielding acetaldehyde and the corresponding hydroxy ketene, the enol of phenylglyoxal. The ketene subsequently reacts with the solvent alcohol to form the new corresponding ester of mandelic acid.[3] In an inert solvent such as benzene, α-keto esters photodecarbonylate with subsequent hydrogen transfer to yield the aldehyde derived from the acid fraction of the ester and the aldehyde or ketone derived from the alcohol portion.[2] It seemed reasonable to us that in the vapor phase, the photochemical behavior of these esters should either approximate behavior in *inert* solvents, or else should indicate extensive radical fragmentation, possibly analogous to pyrolytic pathways.

Experimental

Thermal Decomposition.—Ethyl pyruvate (Aldrich Chemical Co., redistilled) and isopropyl pyruvate (prepared as previously described[2]) in 10- and 20-μl. samples were placed in 5-ml. ampoules, frozen out at Dry Ice temperature, evacuated, and sealed off. The ampoules were then placed in a furnace and heated at the indicated temperatures for the indicated times.

Analyses for condensable products were carried out by gas chromatography on a 6-ft UCON Polar column at 70°. A measured quantity of ether was added for analyses of ethanol, isopropyl alcohol, biacetyl, acetone, and ethyl and isopropyl acetate; methylene chloride was used in the analysis for acetaldehyde. Identification of the various products by retention times was confirmed, in all cases except where trace quantities were involved, by comparison of the infrared spectra of collected samples with those of authentic materials.

Analysis of gaseous products was carried out *via* gas chromatography employing a flame ionization detector.[9] For determination of methane and carbon monoxide at 1.5-ft. Molecular Sieve column (25°) in series with a nickel nitrate (2 ft., 350°) column was employed. Carbon dioxide, ethylene, and ethane were determined employing a 3-ft. silica gel column (25°) in series with the catalytic nickel nitrate column. For propane and propylene a 3-ft. silica gel column at 85° was used.

Photochemical Decomposition.—Fifty-microliter samples of the two esters were placed and frozen out in the cold finger of a 4-l. Pyrex reaction vessel. The vessel was evacuated (in one series of runs 50 mm. of oxygen was added), and the ester was vaporized by heating. The vessel was placed in a Rayonet reactor and the entire assembly was attached to a vacuum system (for a description, see ref. 9). The system was irradiated with light of approximately 3500 Å.; at intervals samples of 1% of the total quantity were removed and analyzed by gas chromatography. Methane and carbon monoxide were determined as in the case of the thermal decomposition. A 3-ft. silica gel column at 25° was employed for analysis of ethylene and propylene. Acetaldehyde and acetone were determined on a 6-ft. tricresyl phosphate column at 60°. Pilot runs in which condensables were sealed off in tubes and analyzed under conditions used

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[1] Photochemistry of α-Keto Acids and α-Keto Esters. IV. Part III is G. F. Vesley and P. A. Leermakers, *J. Phys. Chem.*, **68**, 2364 (1964).

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[3] E. S. Huyser and D. C. Neckers, *J. Org. Chem.*, **29**, 276 (1964).

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[6] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 369.

[7] M. Calvin and R. M. Lemmon, *J. Am. Chem. Soc.*, **69**, 1232 (1947).

[8] N. C. Yang and A. Morduchowitz, *J. Org. Chem.*, **29**, 1654 (1964).

[9] The general procedure has been previously described. See P. A Leermakers and G. F. Vesley, *ibid.*, **30**, 539 (1965).

Table I

Per Cent Yields[a] of Products in Pyrolysis of Ethyl Pyruvate

	Temp., °C.					
	200	250	330	450	450	450
	Time, min.					
	120	120	120	15	30	120
Product	% yield					
Ethylene	0	0	40	44	65	93
Acetaldehyde	5.5	17	13	21	28	17
Ethyl acetate	Trace	Trace	Trace	2.8	4.6	1.4
Ethanol	6.7	25	33	22	33	16
Biacetyl	0	Trace	0.9	2.2	3.5	2.4
Methane	0	0	Trace	13	20	43
Ethane	0	0	Trace	7.8	2.0	3.3
Carbon monoxide	Trace	Trace	7.1	57	81	82
Carbon dioxide	6.8	7.9	38	83	95	90
	Product Mass Balances, %					
C	6.8	18	44	72	97	98
H	8.5	27	53	66	78	98
O	9.1	19	43	92	115	104

[a] (Moles of product/moles of starting material initially present) × 100.

Table II

Per Cent Yields of Products in Pyrolysis of Isopropyl Pyruvate

	Temp., °C.			
	330	450	450	450
	Time, min.			
	120	15	30	120
Product	% yield			
Acetaldehyde	23	30	31	1.7
Acetone	Trace	3.1	2.2	3.8
Isopropanol	9.5	2.6	2.2	2.4
Biacetyl	1.4	2.0	2.1	2.7
Isopropyl acetate	0	0	0	Trace
Methane	1.7	5.2	23	57
Ethane	0	Trace	0	1.9
Ethylene	0	3.7	Trace	9.4
Propane	0.6	1.6	0.7	6.4
Propylene	26	46	45	30
Carbon monoxide	14	20	91	98
Carbon dioxide	12	67	85	90
	Product Mass Balances, %			
C	31	57	73	68
H	34	50	65	58
O	24	65	103	97

for thermal products revealed that no other important products were formed.

Results and Discussion

Thermal Decomposition.—Tables I and II list the products, reaction temperatures, and reaction times in the pyrolytic decomposition of ethyl and isopropyl pyruvate. Mass balances for C, H, and O *in the products* are also included. In the runs where conversion was low, unchanged ester was recovered in quantity almost equal to that which was not accounted for in products. The yield data in the tables are the average of several runs at each temperature and time and are accurate to ± 10%.

It is clear, and contrary to the implication of previous reports,[5,6] that both decarboxylation and decarbonylation occur, and that decarboxylation is the more important primary act of decomposition. The high yields of ethylene from the ethyl ester and propylene from the sopropyl ester, as well as the appearance of carbon dioxide at lower temperatures and shorter times than the appearance of carbon monoxide, bear this out. Equations 1–13 illustrate possible reaction pathways

$$\mathrm{CH_3COCOOCHRCH_3 \longrightarrow CO_2 + CH_3\dot{C}O + \cdot CHRCH_3} \tag{1}$$

$$\mathrm{CH_3COCOOCHRCH_3 \longrightarrow CO + CH_3\dot{C}O + \cdot OCHRCH_3} \tag{2}$$

$$\mathrm{CH_3\dot{C}O + \cdot CHRCH_3 \longrightarrow CH_3CHO + RCH{=}CH_2} \tag{3}$$

$$\mathrm{CH_3\dot{C}O + \cdot OCHRCH_3 \longrightarrow CH_3CHO + RCOCH_3} \tag{4}$$

$$\mathrm{CH_3\dot{C}O + \cdot OCHRCH_3 \longrightarrow CH_3COOCHRCH_3} \tag{5}$$

$$\mathrm{CH_3\dot{C}O \longrightarrow CH_3\cdot + CO} \tag{6}$$

$$\mathrm{CH_3\cdot + \cdot CHRCH_3 \longrightarrow CH_4 + RCH{=}CH_2} \tag{7}$$

$$\mathrm{CH_3\cdot + \cdot OCHRCH_3 \longrightarrow CH_4 + RCOCH_3} \tag{8}$$

$$\mathrm{\cdot OCHRCH_3 + \cdot CHRCH_3 \longrightarrow RCH{=}CH_2 + RCOCH_3} \tag{9}$$

$$\mathrm{2CH_3\dot{C}O \longrightarrow CH_3COCOCH_3} \tag{10}$$

$$\mathrm{2\cdot CHRCH_3 \longrightarrow RCH{=}CH_2 + RCH_2CH_3} \tag{11}$$

$$\mathrm{2\cdot OCHRCH_3 \longrightarrow HOCHRCH_3 + RCOCH_3} \tag{12}$$

$$\mathrm{\cdot CHRCH_3 + \cdot OCHRCH_3 \longrightarrow RCH{=}CH_2 + HOCHRCH_3} \tag{13}$$

(where R = $\mathrm{CH_3}$ or H). Other pathways, such as loss of a hydrogen atom from the acetyl radical to yield ketene (which would subsequently react), to name only one, must exist since the stoichiometry is not fully consistent with eq. 1–13. In the case of the ethyl ester in the 200 and 250° runs, it is difficult to account for the observed stoichiometry by any mechanistic scheme. In addition, it is quite probable that secondary decomposition of the products (especially acetaldehyde) occurs at the higher temperatures. It is interesting to note (without comment) that isopropyl pyruvate is substantially more stable to heat than is the ethyl ester.

Yields of carbon monoxide and methane increase rapidly with temperature, probably resulting from secondary decomposition of acetyl radicals (eq. 6), although some process such as eq. 14 cannot be rigorously excluded.

$$\mathrm{CH_3COCOOCHRCH_3 \longrightarrow \dot{C}H_3 + CO + CO_2 + \cdot CHRCH_3} \tag{14}$$

The most significant findings appear to be the following: (a) in noncatalyzed thermal decomposition of the pyruvates, and quite possibly other α-keto esters as well, initial bond rupture yields *carbon dioxide* rather than carbon monoxide, *such decomposition requiring substantially higher temperatures than previously reported*[5–7] (although, as has been pointed out earlier, the previously reported decomposition *may* have been catalyzed); and (b) recombination is not an important reaction process, the low yields of biacetyl *and ethyl and isopropyl acetates* (as well as other possible recombination products) being indicators of this fact.

Photochemical Decomposition.—Photolysis of the esters resulted in fewer products than were observed in pyrolytic decomposition with decarbonylation rather than decarboxylation being the primary act of fission. Tables III and IV list the per cent yields of various products as a *function of time* at 55° *for ethyl pyruvate, and* the yields for isopropyl pyruvate at 55 and 85° (in the absence and presence of 50 mm. of oxygen at the latter temperature). Irradiation wave length was 3000–3700 Å. Yield data are accurate to ±10%.

TABLE III

PER CENT YIELDS[a] AS A FUNCTION OF TIME IN THE PHOTOLYSIS OF ETHYL PYRUVATE[b]

Time, min.	% yield		
	CO	C_2H_4	CH_3CHO
37	5.4	0.5	16.0
93	12.9		
117		0.6	19.8
326		1.7	21.8
369	38.0		
780	56.1		
1020		4.1	6.6

[a] (Moles of product/moles of starting material initially present) × 100. [b] At approximately 4-mm. pressure; 55°.

TABLE IV

PER CENT YIELDS AS A FUNCTION OF TIME IN THE PHOTOLYSIS OF ISOPROPYL PYRUVATE[a]

Time, min.	% yield				
	CO	C_2H_4	C_3H_6	CH_3CHO	CH_3COCH_3
			55°		
18	0.6	0.1	0.5	0.4	10.9
83		0.2	1.1	1.5	35.1
93	29.6				
162	40.0				
180		0.6	1.7	2.6	60.0
325		0.8	1.3	2.6	49.9
355	50.7				
			85°		
18	3.1	0.1	0.5	0.3	13.2
68	8.1	0.2	0.8	1.6	36.4
193	37.4				
259		0.5	1.2	2.7	53.8
360	54.6				
1030	61.1	0.6	0.3	1.0	59.5
			85°, 50 mm. of oxygen added		
18	b	0.7		0.2	3.0
33		1.0		0.6	22.8
110		0.9		2.6	26.6
173		1.5		3.6	58.7
316		1.5		3.9	59.4
330		2.0		3.2	63.9

[a] At approximately 4-mm. pressure. [b] Carbon monoxide not determinable since oxygen interferred with catalytic conversion to methane for analysis.

During the course of irradiation a film of polymer deposited upon the walls of the reaction vessel which caused the yield of carbon monoxide (the principal product) to level off with time at slightly above 50%. This is probably due to the vessel becoming opaque, and also to the fact that starting material was incorporated into the polymer.

As in the case of the thermal decomposition, it is difficult to give a simple mechanistic picture of the photoreaction. It is apparent, however, that to an extent the photoreaction in vapor phase involves the same primary process as the photolysis in benzene solution, *i.e.*, decarbonylation to yield acyl and alkoxy radicals. The subsequent fate of these radicals, as might be anticipated, is more complex in the vapor phase than in solution due to the lack of immediate vibrational quenching and to the lack of cage effects. In the case of the isopropyl ester, the isopropoxy radicals do seem to produce acetone quite efficiently, but the fate of the acyl portion of the molecule cannot be determined from examination of the products. Presumably most of the acetaldehyde in the photolysis of the ethyl ester, by analogy to the isopropyl ester, derives from the ethoxy portion. The decrease in yield of acetaldehyde at long irradiation times (Table III) is almost surely due to secondary photolysis.

In Table IV one sees that added oxygen appears neither to quench the photolysis nor strongly to influence the formation of acetone. This does not rule out the triplet state as the reactive species (as it is in solution[2]) since decomposition lifetimes could well be shorter than mean lifetimes for collision with oxygen (about 2×10^{-9} sec.). The fact that the yield of acetone is, if anything, increased could result from molecular oxygen assisting the oxidation of isopropoxy radicals to acetone.

In conclusion, there seems to be relatively little correlation between the photochemical and pyrolytic behavior of the pyruvate esters. In both cases the results indicate initial radical fragmentation followed by secondary radical processes, but the fact that the initially formed fragments (carbon dioxide, etc., thermally; carbon monoxide, etc., photolytically) are not the same, would indicate that photochemical decomposition is probably taking place in an electronic excited state and not in a "hot" vibrational level of the electronic ground state. One could, however, argue that such a level could be *very* "hot" in comparison to levels populated by thermal means. If such were the case, though, one would expect less selectivity than is observed in the photochemical reaction where fewer products and virtually no carbon dioxide (which is a major pyrolysis product) are formed.

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