Inorganica Chimica Acta, 31 (1978) 233–236
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

3-Substituted-pentane-2,4-diones: Their Decomposition Patterns and Their Keto–Enol Contents

H. J. HARRIES and G. PARRY
Division of Chemistry and Materials Science, Derby Lonsdale College of Higher Education, Derby DE3 1GB, U.K.
J. BURGESS
Chemistry Department, University of Leicester, Leicester LE1 7RH, U.K.

Received April 11, 1978

Decomposition of 3-substituted-pentane-2,4-diones in aqueous solution is described. Mass spectra of these compounds give fragmentation patterns for gas phase decomposition. Keto–enol ratios are determined from NMR spectra. These structural properties are discussed in terms of substituent effects and solvent participation.

Introduction

Pentane-2,4-dione is a stable compound which forms a large number of complexes with a wide range of metal ions [1, 2]. The physical and chemical properties of this ligand and its complexes have been extensively studied. Much less is known of the 3-substituted 2,4-diones and their metal complexes. It is becoming apparent that some 3-substituted-2,4-diones are considerably less stable than the parent compound. For such relatively unstable ligands, the determination of ligand pK_a values and complex stability constants becomes difficult or impossible.

In this paper, we describe the decomposition of several 3-substituted pentane-2,4-diones in aqueous media. We also report mass spectrometric studies of the ligands, in order to compare the fragmentation patterns in solution and in the gas phase. Keto–enol equilibrium ratios are reported for the ligands.

Experimental

Preparations

The general method involved reaction between pentane-2,4-dione and the appropriate iodo- or bromo-hydrocarbon, using literature procedures. These yield the 3-derivatives: methyl [3], ethyl, propyl, and 1-methylethyl [4]; propen-2-yl [5]. The buten-2-yl derivative was made using pentane-2,4-dione and butanal [6]; the ester ($-COOC_2H_5$) derivative from ethyl-3-oxobutanoate and ethanoyl chloride [7] and the chloro-derivative from pentane-2,4-dione and sulphuryl chloride [8].

Ligand Decomposition

Decomposition was followed spectrophotometrically using the Unicam SP800 with thermostatted cell carrier. Decomposition products were identified by GLC and then estimated by titrimetry (for acid) or uv spectrophotometry (for ketones).

Mass Spectra

These were performed by PCMU (Harwell), under the following conditions: ion-source, temperature 200–400 °C; trap current, 100 μamp: heated inlet system and electron/energy maintained at 70 eV.

NMR Spectra

These were obtained using a Joel 100 MHz instrument using pure liquid samples of ligands and solutions in 50 percent aqueous dioxan (D_2O/d_8-dioxan).

Bromine Titration

The method of Meyer [9] was used to estimate the enol content of solutions of the diketones in methanol. The excess bromine was absorbed using 2,4,4-trimethylpent-1-ene (diisobutylene) as recommended by Cooper and Barnes [10].

Results and Discussion

Stability in Aqueous Media

Pentane-2,4-dione is quite stable in neutral and acidic solutions and decomposes only slowly in alkaline solution [11]. However, some substituted pentane-2,4-diones, including a series of 3-substituted derivatives [12] and some fluoro-derivatives [13], have been found to be less stable. They decompose, especially in alkaline solution at rates fast enough to cause difficulties with ligand pK_a determination and

TABLE I. Half-lives of 3-Substituted Pentane-2,4-diones in Aqueous Media at 298K.

3-Substituent	Half-life/sec.		
	0.05*M* HCl	water	0.05*M* NaCH
H	stable	stable	stable
CH_3	stable	stable	1700
C_2H_5	360	480	1700
$CH_3CH_2CH{=}CH$	540	840	[a]

[a] Half-life could not be measured spectrophotometrically.

TABLE II. Products of Decomposition of 3-Substituted Pentane-2,4-diones in Alkaline Aqueous Medium.

3-Substituent	Products
H[a]	Acetate + propanone
CH_3	Acetate + butanone
C_2H_5	Acetate + pentane-2-one
$CH_2{=}CHCH_2$	Acetate + hex-5-ene-2-one
$CH_3CH_2CH{=}CH$	Acetate + hept-3-ene-2-one[b]

[a] Reference 11. [b] Plus other products, see text.

with estimation of stability constants of their metal complexes.

The products of the alkaline hydrolysis of pentane-2,4-dione are acetone and acetate and kinetic studies have suggested a mechanism [11]. The products and mechanism of alkaline hydrolysis of 3-methylpentane-2,4-dione are analogous.

The stabilities of several 3-substituted pentane-2,4-diones in neutral, acidic and alkaline media are reported in Table I. Stabilities are expressed as half lives for the disappearance of the dione, measured spectrophotometrically. In many cases, half lives are of the order of a few minutes, with obvious consequences in the determination of physical constants.

Products of decomposition of 3-substituted pentane-2,4-diones are shown in Table II. In all cases, including the parent compound, acetate is a major product, confirmed by melting point of the S-benzylthiouronium derivatives. That conversion was close to 100 percent was shown titrimetrically for the 3-ethyl and 3-(1-butenyl) compounds. The ketones produced were characterized by GLC, by comparison of retention times with those of known ketones. Again, the expected ketone gave close to stoichiometric yield in most cases. The yield was determined by uv spectrophotometry using standards of solutions of authentic ketones. The decomposition of the 3-(1-butenyl) derivative whilst giving the expected yield of acetate also gave the expected ketone but in lower than analytical yield; in addition GLC indicated the presence of a dozen other products. Many of these had long retention times suggesting high molecular weights. It is thought unlikely that these additional products are formed by, say, aldol condensation of the ketone since this normally requires strongly alkaline conditions often involving refluxing [14]. Alternatively, they may be formed in situ during GLC (run on polythylene glycol column at 150 °C).

Mass Spectrometry

It is of interest to compare cleavage of 3-substituted pentane-2,4-diones in aqueous solution with their fragmentation in the gas phase. To establish the latter we record the mass spectra in Table III. These vary in complexity depending on substituent and will not be discussed in detail here*. However certain general features are worthy of comment. The mass spectra show that one mode of fragmentation yields

TABLE III. Mass Spectra of 3-Substituted Pentane-2,4-diones. Peaks ⩾ 5% Abundance and m/e ⩾ 53.

Substituent	m/e (relative abundance)
H	43(100), 58(6), 72(7), 85(38), 100(34).
CH_3	43(100), 57(18), 71(22), 72(51), 86(13), 99(20), 114(24)
CH_3CH_2	43(100), 58(6), 71(71), 85(7), 86(32), 100(6), 113(10).
$CH_3CH_2CH_2$	43(100), 58(10) 71(98), 72(8), 100(50), 113(20), 142(6).
$CH_3CH(CH_3)$	43(74), 67(14), 85(100), 86(8), 99(6), 100(40).
$CH_2{=}CHCH_2$	43(100), 44(6), 53(6), 55(12), 79(12), 83(23), 97(52), 98(24), 107(8), 125(7), 140(9).
$CH_3CH_2CH{=}CH$	43(100), 44(8), 58(8), 55(24), 57(7), 58(8), 67(7), 69(21), 77(13), 79(18), 83(15), 84(8), 85(10), 91(7), 93(19), 94(24), 95(8), 97(63), 98(6), 111(16), 112(52), 121(23), 125(40), 136(11), 137(12), 139(16), 154(33), 155(6).
C_2H_5OCO	43(100), 61(13), 69(9), 70(9), 84(17), 85(42), 87(6), 89(6), 98(38) 111(13), 126(25), 127(43), 129(21), 130(13), 143(6), 157(51), 158(7), 172(45), 173(8).
Cl	43(100(, 55(7), 57(5), 91(51), 92(31), 94(12), 99(12), 100(6), 119(73), 121(25), 134(59), 135(6), 136(21).

---

*Copies of proposed fragmentation patterns may be obtained from the authors.

TABLE IV. Positions of Keto $\rightleftharpoons$ Enol Equilibrium for 3-Substituted Pentane-2,4-diones at 298K.

Substituent	Percentage enol			
	Pure liquid[a]		Solutions	
	This work	Previous values	Methanol[b]	50% Aqueous[a] dioxan
H	84	81 to 85[e]	81	40
CH_3	29	28 to 30[f]	1[c]	13
C_2H_5	28	26[g]	1[c]	5
$CH_3CH_2CH_2$	32	27[g]	2[c]	5
$CH_3CH(CH_3)$	0	3[d]	–	–
$CH_2{=}CHCH_2$	43	42[h]	2[c]	5
$CH_3CH_2CH{=}CH$	85	–	8	–
C_2H_5OCO	100	–	82	28
Cl	84	94[j]	83	39

[a] By NMR. [b] By bromine titration. [c] Unreliable, see text. [d] In $CDCl_3$. [e] References 24, 18. [f] References 25, 26. [g] Reference 20. [h] Reference 26. [j] Reference 25.

ketene by cleavage of the same C–C bond whose rupture yields acetate during alkaline hydrolysis in aqueous solution. In both phases, the 3(1-butenyl)-derivative yields a particularly large number of fragments. Other features of all mass spectra are the appearances of methyl and acetyl radicals, of alkenes and of carbon monoxide. The complexity of the mass spectra of these compounds is no doubt partly due to the possibility of keto–enol tautomerism which results in the mass spectra of two similar compounds. This point was noted by Schamp [15] in a study which included examination of the mass spectra of the 3-propyl and 3-(1-methylethyl) derivatives.

Keto $\rightleftharpoons$ Enol Equilibrium

The existence of keto $\rightleftharpoons$ enol equilibria for pentane-2,4-diones and related compounds has long been recognised:

$$CH_3COCHRCOCH_3 \rightleftharpoons CH_3COCRCH(OH)CH_3$$

The position of equilibrium has been studied by both chemical and physical methods. The bromine titration originally proposed by Meyer [16] suffers from the objection that equilibrium may be disturbed by titration. The use of ultraviolet–visible spectrophotometry [17] assumes that molar extinction coefficients are unaffected by the solvent; the method is often calibrated by a bromine titration. More recently, NMR has become widely used [18] and gives good results although we have found discrepancies of a few percent when ratios are determined using protons in different parts of the molecule. The effect of solvent and temperature on the equilibrium may be examined by this method [19].

Table IV gives the percentage enol form in 3-substituted-pentane-2,4-diones in the liquid state, in methanol solution and 50 percent (v/v) aqueous dioxan. Methanol results were obtained by bromine titration and appear surprisingly low in cases of low enol content. The other results were obtained by NMR. The (1-methyl)ethyl derivative appears to have the lowest enol content of the 3-substituted derivatives and is in accord with an earlier report of less than 3 percent enol in the liquid state [20].

The position of the keto–enol equilibrium is affected by several factors, particularly electronic and steric effects of the substituents and the nature of the solvent. Electron-releasing alkyl groups in the 3-position decrease the enol content, while the electron withdrawing effects of the ester and chloro groups causes increasing enol content. Ault [21] has shown a relationship between pK_a and enol content for these alkyl derivatives. However, there are indications of steric factors in the extreme case of the 3(1-methyl) ethyl-derivative. That the nature of the solvent should affect the position of keto–enol equilibrium can be understood in the light of the strong tendency of the enol-form to H-bond internally while the keto-form may H-bond to protonic solvents, which should thus stabilize the keto-form. This is shown by comparing results for pure liquids with those in 50 percent aqueous dioxan (Table IV). The change from pure liquid to aqueous dioxan is accompanied by an increase of dielectric constant. Pure pentane-2,4-dione has a dielectric constant of 25.7 [22] while the value for 50 percent aqueous dioxan is estimated as 34 from data of Harned and Owen [23]. This increase of enol content with decrease of dielectric constant has been stressed by Ault [21] who surveyed the enol content of pentane-2,4-dione in a range of solvents from cyclohexane (dielectric constant 2.0; enol content 95 percent) to water (dielectric constant 78.5; enol content 15 percent).

References

1 L. G. Sillen and A. E. Martell, "Stability Constants of Metal Ions Complexes", Chemical Society Special Publications 17 (1964) and 25 (1971).
2 J. Stary, "Solvent Extraction of Metal Chelates", Pergamon, London (1964).
3 A. W. Johnson, E. Markham, and R. Price, *Org. Synth., 42,* 75 (1962).
4 T. M. Shepherd, *Chem. and Ind.,* 567 (1970).
5 R. B. Davis and P. J. Hurd, *J. Am. Chem. Soc., 77,* 3284 (1955).
6 G. B. Payne, *J. Org. Chem., 24,* 1830 (1959).
7 A. Spassow, *Org. Synth., 3,* 390 (1955).
8 A. M. Tanaka, T. Shono and K. Shinra, *Bull. Chem. Soc. Japan, 42,* 3190 (1969).
9 K. H. Meyer, *Ann. Physik., 380,* 212 (1911); *Chem. Ber., 45,* 2843 (1912).
10 S. R. Cooper and R. P. Barnes, *Ind. Eng. Chem. (Anal. Edn.), 10,* 379 (1938).
11 J. P. Calmon and P. Maroni, *Bull. Soc. chim. France, 9,* 3761 (1968).
12 J. L. Ault, J. Burgess and H. J. Harries, *Inorg. Chim. Acta, 25,* 65 (1977).
13 H. T. Daniel, private communication.
14 J. B. Conant and N. Tuttle, *Org. Synth., 1,* 199 (1944).
15 N. Schamp, M. Vanderwalle and M. Francque, *Bull. Soc. Chim. Belges, 76,* 528 (1967).
16 K. H. Meyer, *Ann. Physik., 380,* 212 (1911).
17 P. Grossman, *Z. Physik. Chem., 109,* 305 (1924).
18 H. Jarrett, M. Sadler and J. Shoolery, *J. Chem. Phys., 21,* 2092 (1953).
19 L. Reeves, *Canad. J. Chem., 35,* 1351 (1957).
20 Y. N. Molin *et al., Bull. Acad. Sci. USSR.,* 1523 (1965).
21 J. L. Ault, *Ph.D. Thesis,* University of Leicester (1973).
22 "Handbook of Chemistry and Physics", Chemical Rubber Publishing Company (1965).
23 H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold, New York (1950).
24 H. Koshimura, J. Saito and T. Okuba, *Bull. Chem. Soc. Japan, 46,* 632 (1973).
25 J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc., 86,* 2105 (1964).
26 G. Allen and R. A. Dwek, *J. Chem. Soc. B,* 161 (1966).