

THE LIQUID PHASE PHOTOLYSIS OF 1,4-DIBROMO-2,3-BUTANEDIONE

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Summary

The liquid phase photolysis of 1,4-dibromo-2,3-butanedione ($(\text{CH}_2\text{-BrCO})_2$) was investigated at different wavelengths and in various solvents. In ethanol the major products are $\text{CH}_3\text{COCOCH}_2\text{Br}$, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$, $\text{CH}_3\text{-COOC}_2\text{H}_5$ and $\text{CH}_2\text{BrCOOC}_2\text{H}_5$. Of these compounds only $\text{CH}_3\text{COCOCH}_2\text{Br}$ is a primary photolysis product originating via hydrogen atom abstraction from $\text{CH}_3\text{CH}_2\text{OH}$ by the excited $(\text{CH}_2\text{BrCO})_2$ molecule. The $\text{CH}_3\dot{\text{C}}\text{HOH}$ radical thus formed is the probable precursor of $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$. It is suggested that the observed esters, which are formed in a 1:1 ratio, are produced by the photolysis of the α -oxo-hemiacetal which is formed by the reaction of $(\text{CH}_2\text{BrCO})_2$ with ethanol.

1. Introduction

The liquid phase photolysis of biacetyl ($(\text{CH}_3\text{CO})_2$) has been extensively investigated. It is generally accepted that, especially at long wavelengths, the major reaction products originate from hydrogen atom abstraction by the excited biacetyl molecule from a suitable RH compound [1 - 3]. Similar results have been reported for the photolysis of $(\text{CF}_3\text{CO})_2$ [4]. It seemed interesting to study the photolysis of 1,4-dibromo-2,3-butanedione ($(\text{CH}_2\text{-BrCO})_2$) from a comparative standpoint to observe the effect of the bromine substituent on the primary process and to observe the behavior of the bromine-substituted radicals produced by the primary process.

2. Experimental

The $(\text{CH}_2\text{BrCO})_2$ was obtained from Aldrich Chemical Co. and was not further purified since mass spectrometric and gas chromatographic analyses did not detect any impurities.

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Most irradiations were carried out with 0.1 M solutions in vials of approximately 2 ml in type RPR-208 Rayonet photochemical reactors equipped with 253.7, 313 or 366 nm lamps. A carousel-type apparatus was used to ensure that simultaneous irradiations would provide equal doses to each sample. The duration of the exposures varied from about $\frac{1}{2}$ to 2 h. Some irradiations were carried out with a Philips SP-500 W mercury lamp and a "403 nm" glass filter. The duration of these exposures varied from 12 to 24 h. All the solutions were deaerated by bubbling helium through them for about 10 min prior to exposure to light.

At each wavelength some irradiations were carried out in the presence of free radical scavengers. The scavengers used were *cis*-1,3-pentadiene (which is also a known triplet quencher), C_6H_5Br and C_2H_5Br . Although C_6H_5Br and C_2H_5Br are not free radical scavengers as such, if they are photolyzed they provide bromine atoms and C_6H_5 or C_2H_5 radicals which, if produced in large enough concentrations, should trap the free radicals produced in the system.

3. Results and discussion

Table 1 shows the products and their distribution as a function of the energy of the incident light obtained with a 0.1 M solution in ethanol at less than 10% conversion. Although the data represent average values of two or more experiments at each wavelength it must be pointed out that the acetal data especially are subject to large errors. This compound is very unstable and its capacity to survive the passage through the gas chromatograph columns depended very much on the "freshness" of the columns. For this reason the formation of acetal was investigated exclusively in ethanol solutions. It was the only product which could be completely suppressed by free radical scavengers. The fact that $CH_3CH(OC_2H_5)_2$ and not $CH_2BrCH(OC_2H_5)_2$ is formed indicates that the acetal is produced exclusively from the solvent molecule ethanol and that the photolysis of $(CH_2BrCO)_2$ only creates the

TABLE 1

Product distribution^a as a function of wavelength in the photolysis of a 0.1 M solution of $(CH_2BrCO)_2$ in ethanol

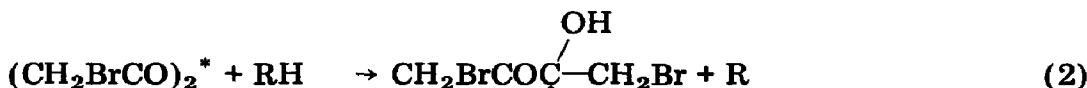
Product	Wavelength (nm)			
	400	366	300	254
$CH_3CH(OC_2H_5)_2$	3.5	2.0	0.6	trace
$CH_2BrCOCOCH_3$	1.0	1.0	1.0	1.0
$CH_3COOC_2H_5$	0.6	3.5	1.6	0.7
$CH_2BrCOOC_2H_5$	0.8	4.2	1.8	0.6

^aRelative to the production of $CH_2BrCOCOCH_3$.

conditions favorable for its production. One of these conditions is probably the production of the $\text{CH}_3\dot{\text{C}}\text{HOH}$ radical. It is well established in the literature that the acid catalyzed addition of alcohols to aldehydes leads to hemiacetals and to acetals, even though the intricate details of these additions are by no means clear.

The only primary product of the photolysis of $(\text{CH}_2\text{BrCO})_2$ was $\text{CH}_2\text{-BrCOCOCH}_3$. This compound was observed in all solvents even though its production was minute in CH_3CN solution. Simultaneous exposures of 0.1 M solutions in CH_3CN , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ gave the following comparative yields of $\text{CH}_2\text{BrCOCOCH}_3$: 1.0 in CH_3CN , 13.0 in $\text{C}_2\text{H}_5\text{OH}$ and 31.0 in $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. These data indicate that the rate of $\text{CH}_2\text{BrCOCOCH}_3$ production increases with the ease with which the C—H bond of the solvent can be broken. These data compare well with the activation energies of 10, 9.6 and 8.0 kcal mol⁻¹ for the hydrogen atom abstraction by methyl radicals from CH_3CN [5, 6], $\text{C}_2\text{H}_5\text{OH}$ [7] and $\text{C}_2\text{H}_5\text{OCH}_3$ [8, 9] respectively.

The most likely mechanism to explain the formation of $\text{CH}_2\text{BrCOCOCH}_3$ is as follows:



The excited parent molecule abstracts a hydrogen atom from ethanol and produces the $\text{CH}_3\dot{\text{C}}\text{HOH}$ radical (which is the precursor to the acetal) and the bromine-substituted dimethyl semidione radical. Although unsubstituted dimethyl semidione radicals are quite stable [10, 11], it is expected that the bromine-substituted radical may decompose readily according to reactions (3) and (4) since the C—Br bond is about 30 kcal mol⁻¹ weaker than the corresponding C—H bond. The observation that the production of $\text{CH}_2\text{BrCOCOCH}_3$ is not, or only to a minute extent, reduced by the addition of free radical scavengers agrees with this mechanism.

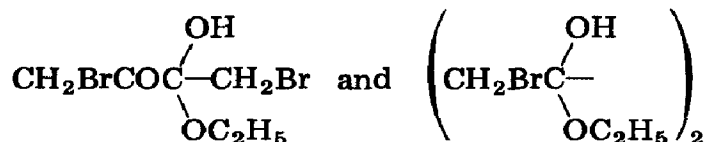
Finally, we have to consider the formation of bromine-substituted and unsubstituted esters (see Table 1). Although there is some scatter (probably because of the difficulty in separating $\text{CH}_3\text{COOC}_2\text{H}_5$ from the large excess of ethanol), the two esters seem to be produced in approximately equal amounts and their production is completely independent of the presence or absence of free radical scavengers. The esters are also observed if trace amounts of ethanol are added to CHCl_3 or CH_3CN solutions of $(\text{CH}_2\text{BrCO})_2$ but are not produced in the absence of ethanol. Although the esters were not produced in blank experiments (which had been kept in the dark for 24 h or more) it seems likely that they originate from the photolysis of one or more

TABLE 2

Photolysis of $(\text{CH}_2\text{BrCO})_2$: ratios of ester formation in various alcohol mixtures

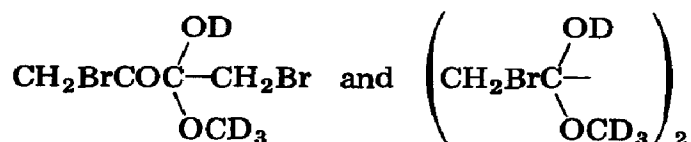
Solvents		$\text{CH}_2\text{BrCOOR}^1/\text{CH}_2\text{BrCOOR}^2$
$R^1\text{OH}$	$R^2\text{OH}$	
$\text{C}_2\text{H}_5\text{OH}$	CH_3OH	0.78
$1\text{-C}_3\text{H}_7\text{OH}$	CH_3OH	0.77
$1\text{-C}_5\text{H}_{11}\text{OH}$	CH_3OH	1.80
$2\text{-C}_3\text{H}_7\text{OH}$	CH_3OH	0.14
$2\text{-C}_5\text{H}_{11}\text{OH}$	CH_3OH	0.12
$t\text{-C}_4\text{H}_9\text{OH}$	CH_3OH	very small
$1\text{-C}_3\text{H}_7\text{OH}$	$\text{C}_2\text{H}_5\text{OH}$	1.14
$1\text{-C}_5\text{H}_{11}\text{OH}$	$2\text{-C}_3\text{H}_7\text{OH}$	11.70

compounds arising from a reaction between ethanol (or other alcohols) and $(\text{CH}_2\text{BrCO})_2$. The possible compounds are the hemiacetals



Neither compound is expected to be observed by gas chromatographic analysis since it would decompose before reaching the detector.

Figure 1 shows the variation with time of the UV spectrum of $(\text{CH}_2\text{BrCO})_2$ in ethanol. As expected the spectrum at $t = 0$ (the time at which the $(\text{CH}_2\text{BrCO})_2$ was dissolved in ethanol) closely approximates the spectrum of biacetyl in the gas phase [12] which has maxima at about 420 and 270 nm. The decrease of the 420 nm peak with time on standing in the dark is similar to the decrease observed [13] in the corresponding peak of $(\text{CH}_3\text{CO})_2$ on photolysis of a solution of $(\text{CH}_3\text{CO})_2$ in 2-propanol. Thus the decreases with time of the maxima at 420 nm and at 290 nm indicate a decrease in the free $(\text{CH}_2\text{BrCO})_2$ concentration. It is clear that if the concentration of $(\text{CH}_2\text{BrCO})_2$ decreases in alcoholic solutions a new compound must be formed by reaction of $(\text{CH}_2\text{BrCO})_2$ with the alcohol, even though we do not observe any positive evidence in the UV spectrum for such a compound. However, nuclear magnetic resonance analyses of solutions of $(\text{CH}_2\text{BrCO})_2$ in CD_3OD confirm the presence of both of the hemiacetals



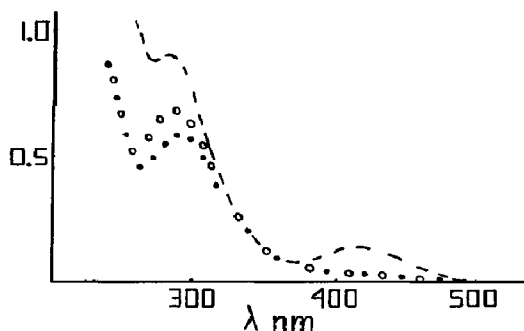
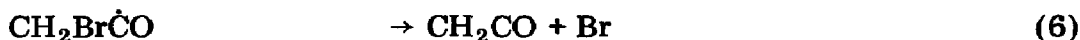
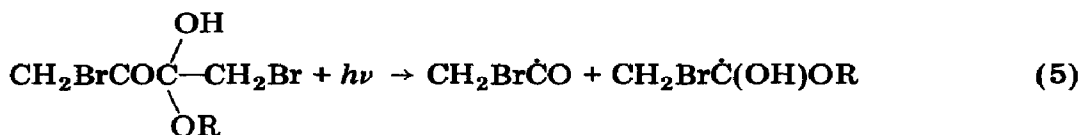


Fig. 1. UV spectrum of $(\text{CH}_2\text{BrCO})_2$ (0.0075 M) in ethanol taken at various intervals: ---, $t = 0$; $\circ \circ \circ$, $t = 80$ min; $\bullet \bullet \bullet$, $t = \infty$.

Therefore our assumption that the esters may be formed by photolysis of the hemiacetals seems justified.

Because the latter hemiacetal will not absorb radiation of the wavelengths used in this investigation, it may be rejected as the compound responsible for the formation of the esters. The photoformation of the two esters in an approximately 1:1 ratio may now be represented by the following, somewhat speculative, sequence:



Since free radical scavengers had no effect on the yields of the esters it must be assumed that reactions (6) and (8) occur within the solvent cage. This cage effect is perhaps better understood if we realize that the products of reactions (6) and (8) might be formed directly by a type of disproportionation reaction between the $\text{CH}_2\text{Br}\dot{\text{C}}\text{O}$ and $\text{CH}_2\text{Br}\dot{\text{C}}(\text{OH})\text{OR}$ radicals produced by reaction (5). Our observation regarding the formation of hemiacetals in alcoholic solutions is further confirmed by literature data which indicate that, in methanol solutions, 80% of the unsubstituted biacetyl is in the hemiacetal form [14]. As expected, in methanol solutions we observed the products $\text{CH}_3\text{COOCH}_3$ and $\text{CH}_2\text{BrCOOCH}_3$ in approximately equal quantities. However, it was often not possible to separate quantitatively the unsubstituted ester from the large amounts of alcohol used as solvent. Therefore, in a series of experiments with various alcohols, we analyzed only for the bromo-substituted ester. This series was carried out with 0.1 M solutions of $(\text{CH}_2\text{BrCO})_2$ in equimolar mixtures of two alcohols. Table 2 gives the results of these experiments. Accepting that the rates of ester formation

reflect the concentration ratios of the various hemiacetals, we note that the hemiacetal formation is much more pronounced for primary alcohols than for secondary alcohols. This may be explained by a steric effect since the oxygen in secondary alcohols is much more shielded than in primary alcohols. If so, we would expect even less reaction with t-butanol as is indeed observed. Finally it should be noted that the ester ratios in the various alcohol mixtures did not vary with exposure time or with storing time of the samples before exposure. This indicates that the equilibrium concentration of the hemiacetals may possibly be light catalyzed.

In conclusion it may be stated that the liquid phase photolysis of $(\text{CH}_2\text{BrCO})_2$ is very similar to that of $(\text{CH}_3\text{CO})_2$. Minor decomposition products (such as CH_3CO and CO in the photolysis of biacetyl) may also be formed in the photolysis of $(\text{CH}_2\text{BrCO})_2$. The fact that we did not observe any such products may be due simply to the fact that we operated at low conversions. Hydrogen atom abstraction in the presence of RH compounds by the excited dione molecule is the main primary process for both diketones.

Acknowledgments

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