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Chemistry of Ultrasound. II. Irradiative Behavior of Aliphatic Aldehydes and Carboxylic Acids in an Aqueous Medium

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Abstract: The 800-kHz irradiations of homologous series of aliphatic aldehydes and carboxylic acids were effected in aqueous solution or suspension. A gaseous atmosphere of argon was employed for most irradiations; however, a few runs were conducted under oxygen. Rates of gas evolution were measured for argon runs and gas consumption was measured for the oxygen cases. In general, gas evolution or consumption was fairly insensitive to compound type or structure. Gases evolved included carbon monoxide, carbon dioxide, methane, ethylene, acetylene, and ethane. Relative proportions of these products depended most strongly on the functional group present and to a lesser extent on the length and structure of the carbon chain. From analyses of the solution products it was seen that two reaction pathways exist for the aldehydes, oxidation to the corresponding carboxylic acid and fragmentation to smaller carboxylic acids with concurrent formation of the one- and two-carbon gases. For the carboxylic acids only the latter, less favored, process is available. Irradiations of a homologous series of hydrocarbons indicated that only those saturated compounds above butane in chain length and only those olefins above ethylene in chain length are subject to fragmentation in an aqueous medium. Sonolyses of butanoic acid and butanal in D_2O indicated that extensive exchange of the α hydrogens with solvent hydrogens occurs for both compounds and, for butanal, exchange also occurs at the carbonyl carbon. Similar treatment of α,α-dideuteriobutanoic acid in H_2O confirmed the exchange observation and demonstrated, through a retardation in gas evolution rate, the importance of α-hydrogen abstraction to the fragmentation process. The sites for initiation of the ultrasonic oxidation and fragmentation and some of the intermediates of fragmentation are suggested by the results obtained.

In the previous paper of this series[2] we outlined the basic principles and several current theories on the action of ultrasound on simple molecular species.[3] In particular, we were interested in the behavior of water as a solvent and reactant under various irradiation conditions, since it was the medium in which the remainder of the work described in that paper, and this one, was performed. Subsequent to our studies of water irradiations we turned to investigations of aqueous solutions of carbon tetrachloride and aqueous solutions of di-*n*-butyl sulfide. It is as a direct consequence of the latter, sulfide irradiations, that the presently described work was undertaken.

Upon irradiation of di-*n*-butyl sulfide (1) we noted

$$\underset{\mathbf{1}}{n\text{-Bu}_2\text{S}} \xrightarrow[\text{H}_2\text{O, Ar}]{800\text{ kHz}} \underset{\mathbf{2}}{n\text{-Bu}_2\text{SO}} + \underset{\mathbf{3}}{n\text{-BuSO}_3\text{H}} + \underset{\mathbf{4}}{\text{PrCOOH}} + \text{CO} + \text{CH}_4 + \text{CH}_2\text{=CH}_2 + \text{HC}\equiv\text{CH}$$

that in addition to the major sulfoxide product, **2**, there existed *n*-butanesulfonic acid (**3**) and traces of butanoic acid (**4**) as by-products in the irradiated solution. Since the amount of the carboxylic acid in no way matched that of the sulfonic acid, it was apparent that a major portion of the alkyl fragments removed during formation of **3** was lost to the atmosphere above the irradiated column. Analysis of this gaseous atmosphere revealed, in addition to the initially saturating argon, carbon monoxide, methane, ethylene, and acetylene. In control experiments with di-*n*-butyl sulfoxide (**2**), di-*n*-butyl sulfone, butanal, and butanoic acid it was shown that these compounds also afforded the same gaseous fragments at similar evolution rates but, with the exception of butanal, in somewhat different ratios. The mechanistic conclusion drawn from these observations

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(1) Abstracted in part from the Ph.D. thesis of S. B. Reifsneider, Brown University, 1972.

(2) L. A. Spurlock and S. B. Reifsneider, *J. Amer. Chem. Soc.*, **92**, 6112 (1970).

(3) The most extensive review of this subject is included in "Ultrasound, Physical Chemistry and Biological Effects," E. I. El'piner, Ed., Consultants Bureau, New York, N. Y., 1964.

was that the aldehyde serves as a probable precursor to the fragments observed in irradiations of **1** and is therefore a transient intermediate in the overall reaction scheme.[2]

Aside from the mechanistic deductions which it afforded, the intriguing features of this fragmentation pathway were the dependence of the ratio of fragment gases on the functional group present in the original molecule and the almost insignificant variation in the rates of gas evolution from the several compound types studied. These led us to examine the fragmentations in more detail, with particular emphasis on establishing a probable mode of initiation and on identification of intermediates leading to the fragments in the gas and solution phases.

As the efficiencies of butanal and butanoic acid in the fragmentation reaction had already been established through our control experiments, and since it was clear that this seemingly slight variation in functional group caused large changes in the gaseous product ratio, it was decided to begin the study with simple aliphatic carboxaldehydes and carboxylic acids. This study had the additional virtue of being the first systematic study of simple aliphatic functional group types, in which most of the homologs were examined for solution and gaseous products. Placing the arbitrary limit of ten carbons on our investigations we therefore conducted a thorough study of the ultrasonic irradiative behavior of most unbranched and a few branched or doubly functionalized aliphatic acids and aldehydes in aqueous solution or suspension.

Results

Generally irradiations were conducted at 800 kHz with 9.4-W/cm^2 intensity, a gross solution temperature of 25°, and an argon atmosphere. A few runs were also performed with an oxygen atmosphere.[4] Rates of gas evolution (or consumption, for oxygen runs) were followed by means of a gas buret attached to the irradiation vessel. The rates of evolution are shown in Table I and are zero-order values derived from the slopes of gas moles evolved *vs.* time plots. Results for each compound are the averages of at least two individual runs with a minimum of eight observations per run. The qualitative analyses of the gaseous products, carbon monoxide, carbon dioxide, methane, ethane, ethylene, and acetylene were accomplished with infrared spectroscopy. Quantitative analyses were effected with gas chromatography. The gaseous product distributions are displayed in Table II.

Table I. Rate Studies of Gas Evolution during 800-kHz, 9.4-W/cm^2 Irradiations of 0.006 *M* Aqueous Solutions of Aldehydes and Acids at 25°

Compound	$k \times 10^5$, mol/min	Compound	$k \times 10^5$, mol/min
Methanal	1.77 ± 0.09	Ethanoic acid	0.46 ± 0.04
Ethanal	5.39 ± 0.04	Lactic acid	0.68 ± 0.04
Propanal	2.76 ± 0.10	Pyruvic acid	0.86 ± 0.03
Butanal	3.36 ± 0.02	Acrylic acid	0.98 ± 0.02
2-Methylpropanal	2.56 ± 0.17	Propanoic acid	1.18 ± 0.01
		Butanoic acid	2.57 ± 0.04
Pentanal	1.29 ± 0.06	2-Methylpropanoic acid	2.63 ± 0.07
Hexanal	1.30 ± 0.09		
Octanal	1.18 ± 0.06		
Decanal	1.82 ± 0.06	Pentanoic acid	1.63 ± 0.06
Methanoic acid	0.18 ± 0.05	Hexanoic acid	1.58 ± 0.03
		Octanoic acid	2.55 ± 0.12
		Decanoic acid	2.13 ± 0.04

Table II. Composition of Gas Mixtures Evolved during 800-kHz, 9.4-W/cm^2 Irradiations of 0.006 *M* Aqueous Solutions of Aldehydes and Acids at 25°

	Relative proportions					
Compound	CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2
Methanal	78	22				
Ethanal	59	1	29		4	7
Propanal	63	1	25	3	5	2
Butanal	41	1	35	5	14	4
2-Methylpropanal	41	1	42	6	8	2
Pentanal	41	1	39	5	11	3
Hexanal	42	1	40	4	9	4
Octanal	39	1	38	5	10	7
Decanal	67	1	18	Tr	6	8
Methanoic acid	65	35				
Ethanoic acid	88	6	6			
Lactic acid	96	1	3			
Pyruvic acid	100					
Acrylic acid	94	3	3		Tr	Tr
Propanoic acid	90	1	8	0.3	0.3	0.3
Butanoic acid	73	2	16	2	3	4
2-Methylpropanoic acid	76	2	15		2	5
Pentanoic acid	73	Tr	21	2	2	2
3-Methylbutanoic acid	65	1	25	Tr	3	6
Hexanoic acid	52	11	24	Tr	7	6
Octanoic acid	43	2	30		13	12
Decanoic acid	69	Tr	19		5	7

After a work-up of extraction techniques which afforded material returns of 50–90% for 3-hr irradiations, gas chromatographic techniques were also used for identification and quantitative measurements of most of the solution components shown in Tables III and IV. The exceptions in this case occurred with irradiations of methanal and ethanal (Table III), where the corresponding acids, formed as products, were determined titrimetrically to overcome the inefficiencies of the extraction techniques. In partial explanation of occasional poor material balances, it was noted that in these cases a yellow insoluble polymeric substance was also formed. Physical examination and infrared spectral analyses[5] indicated this polymer to be a polyacetylene, and introduced the notion that the values for acetylene proportion listed in Table II are probably inaccurate, due to this subsequent transformation of the primary product.

To check this and to ensure that none of the other observed fragments were reacting further, the product gases shown in Table II were subjected to irradiation in an argon–water system under conditions identical to those from which they were evolved. All were completely stable to these conditions with the anticipated exception of acetylene, which polymerized very rapidly to the aforementioned yellow insoluble solid material.

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(4) See ref 10 for a detailed description of the irradiation apparatus.

(5) The polymer created by irradiation of acetylene in argon saturated water, and this polymer, possessed identical infrared spectra with a characteristic absorption band at 3300 cm^{-1}.

Table III. Product Studies during 800-kHz, 9.4-W/cm^2 3-Hr Irradiations of 0.006 *M* Aqueous Solutions of Aldehydes at 25°

Aldehyde	Relative proportions: RCHO	$C_2H_4O_2$	$C_3H_6O_2$	$C_4H_8O_2$	$C_5H_{10}O_2$	$C_6H_{12}O_2$	$C_7H_{14}O_2$	$C_8H_{16}O_2$	$C_9H_{18}O_2$	$C_{10}H_{20}O_2$
Methanal	76									
Ethanal	78	22								
Propanal	75	13	12							
Butanal	60	17	Tr	22						
2-Methyl-propanal	78	Tr	Tr	22						
Pentanal	50	5	1	4	40					
Hexanal	47	5	2	1	3	42				
Octanal	40	4	8		4	2	2	40		
Decanal	80	1	Tr	2	2	4		Tr		11

Table IV. Product Studies during 800-kHz, 9.4-W/cm^2, 3-Hr Irradiations of 0.006 *M* Aqueous Solutions of Carboxylic Acids at 25°

Acid	Relative proportions: $C_2H_4O_2$	$C_3H_6O_2$	$C_4H_8O_2$	$C_5H_{10}O_2$	$C_6H_{12}O_2$	$C_7H_{14}O_2$	$C_{18}H_{16}O_2$	$C_9H_{18}O_2$	$C_{10}H_{20}O_2$
Propanoic	Tr	100							
Butanoic	3	5	92						
2-Methyl-propanoic	4	5	91						
Pentanoic	Tr	Tr	2	98					
2-Methyl-butanoic	2	1	2[a] 7[b]	88[b]					
Hexanoic	Tr	Tr	1	4	95				
Octanoic	1	1	9	1	1		87		
Decanoic	5	2	7	4	13		3		65

[a] Butanoic acid. [b] Methylpropanoic acid.

In an effort to trace probable precursors of the fragmentation products several hydrocarbons were subjected to these argon–water irradiations. Rates of gas evolution and gaseous product distributions are shown in Table V. The only product isolated from the aqueous phases of these irradiations was an unidentifiable polymeric material which occurred in low yield.

Table V. Rate Studies and Composition of Gas Mixtures Evolved during 800 kHz, 9.4-W/cm^2 Irradiations of Hydrocarbons in Aqueous Suspension at 25° under Argon

Compounds	$k \times 10^5$, mol/min	Relative proportions: CO	CO_2	CH_4	C_2H_6	C_2H_4	C_2H_2
n-Hexane	1.68 ± 0.01	29		39			18
n-Pentane	1.42 ± 0.04	21	Tr	33	10	23	13
n-Butane	*b*						
1-Butene	2.49 ± 0.11	Tr		63	13	12	12
Propane	*b*						
Propene	*a*	Tr		67		25	8
Ethane	*b*						
Ethylene	*b*						
Methane	*b*						

[a] No change in the atmospheric volume was detected. [b] Inert.

An exception to this occurred with propene which reacted rapidly to give a copious polymer which was, at least in part, polyacetylene. It should also be pointed out that while the rate of gas evolution was not measurable from irradiations of propene, the formation of gaseous products was nevertheless quite rapid. Gas samples from the irradiations, when analyzed by gas chromatography, showed the products indicated in Table V in high concentration.

In an attempt to elucidate the mechanism of the fragmentation process under sonolysis, samples of *n*-butanoic acid and *n*-butanal were irradiated in 99% D_2O saturated with argon, under conditions similar to those described earlier. Control experiments with identical solution volumes in H_2O were also effected. Rates of gas evolution were measured and the product gases were analyzed by gas chromatography and mass spectrometry. The results from these measurements are shown in Table VI. The values were obtained in the same manner as was previously described for runs in water. The butanoic acid and butanal recovered from sonolysis in D_2O were also analyzed by mass spectrometry.

In the case of butanal, the recovered material after 3 hr of irradiation showed substantial (>sevenfold) increases in the relative proportions of mass spectral fragments at *m/e* 73, 58, and 45 as compared to those observed from the unirradiated material. These correspond to the monodeuterated M^+, $(M - 15)^+$, and base peaks, respectively, and indicated that at least one hydrogen atom had been partially replaced by a deuterium atom. On the basis of the fragment ions in which deuteration was observed, it could be concluded that the point of deuteration was either the α carbon or the carbonyl carbon, or both.[6] Our instrumental sensitivity did not allow unequivocal differentiation between these possibilities.

The situation was somewhat clearer in the butanoic acid–D_2O irradiations. In this case the recovered acid after a 3-hr irradiation showed greater than threefold increases in the relative proportions of mass spectral fragments at *m/e* 89, 74, and 61 over those from the unirradiated acid. These again correspond to the

[6] The possibility of deuteration at the γ carbon can be discarded due to the observed deuteration of the $(M - 15)^+$ ion, in which this carbon is no longer present. A similar argument may be used to eliminate the β carbon as a point of deuterium attachment if one may assume that this carbon is lost in the McLafferty rearrangement affording the still deuterated *m/e* 45 fragment ion.

Table VI. Rates of Gas Evolution and Gaseous Product Distributions from Sonolyses of *n*-Butanal and *n*-Butanoic Acids

				Relative proportions						
Compound	Medium	Volume, ml	$k \times 10^5$, mol/min	CO	CO_2	CH_4[a]	CH_3D	C_2H_6[b]	C_2H_4[b]	C_2H_2[b]
Butanoic acid	H_2O	150	0.54 ± 0.05							
	D_2O	150	1.08 ± 0.14	72	2	8	8	2	3	5
	H_2O	100	0.83 ± 0.03							
	D_2O	100	1.66 ± 0.08							
α,α-Dideuterio-butanoic acid	H_2O	300	1.60 ± 0.08	74	1	8	8	2	3	4
Butanal	D_2O	150	1.16 ± 0.14	44		31	4	4		3

[a] May include small amounts of polydeuterated material undetectable by the experimental method. [b] Includes deuterated hydrocarbons undetectable by the mass spectrometer utilized.

Table VII. Rate Studies of Oxygen Consumption and Product Studies from 800-kHz, 9.4-W/cm² Irradiations of 300-mg/300-ml Aqueous Solutions at 25°

		Relative proportions									
			Carboxylic acids								
Compound	$k \times 10^5$, mol/min	Starting material	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
Propanoic acid	6.25 ± 0.28	87	13	87							
Butanoic acid	6.52 ± 0.26	95	3	2	95						
Sodium butanoate	3.69 ± 0.11	96	3	1	96						
2-Methylpropanoic acid	5.54 ± 0.27	*a*									
Decanoic acid	7.81 ± 0.05	99	0.2	0.4	0.1						99
Propanal	7.53 ± 0.37	44	16	40							
Butanal	7.55 ± 0.28	26	32		38						
Decanal	11.4 ± 0.12	14	1	1	5	3	2	Tr	4		70

[a] Solution products not examined.

monodeuterated M^+, $(M - 15)^+$, and base peaks, respectively, and showed a tendency for exchange of a single hydrogen for a deuterium from the solvent. Replacement of the –OH proton could be eliminated from consideration since the workup of the irradiated sample would have caused rapid exchange of any deuterium for hydrogen at this reactive site. The deuterium observed in the mass spectral ions must therefore be attached to a carbon, and utilizing prior logic (see ref 6), it must be at the α carbon.

In further substantiation of this result, a solution of α,α-dideuteriobutanoic acid in H_2O was subjected to ultrasonic irradiation under an argon atmosphere with conditions similar to those utilized earlier. The rates of gas evolution and composition of gaseous products are shown in Table VI. Interestingly, the rate of gas evolution was only 62% of that for the undeuterated material under the same conditions (see Table I) while the gaseous product distribution was nearly identical to that from irradiation of undeuterated acid in D_2O. The recovered acid from a 5-hr irradiation showed at least fourfold increases in mass spectral fragment ions at *m/e* 74, 73, 61, and 60. These correspond to mono- and undeuterated $(M - 15)^+$ and base ions, and suggested by their loss of the α deuteria that the exchange process observed in the D_2O irradiations does indeed occur at the α carbon.

Finally, variation of an experimental parameter of irradiation, the gaseous atmosphere, was investigated. A series of eight compounds was irradiated under conditions identical to those described previously except for use of oxygen as the saturating gas. Under these conditions gaseous fragmentation products were never detected, and gas consumption resulted in the only observable change in the atmosphere above the irradiated column. The rate of oxygen consumption during irradiation of each compound is shown in Table VII. In the aqueous phase of the reaction only carboxylic acids were formed irrespective of the starting compound. Material balances varied from 70 to 92%, except for the lower molecular weight aldehydes where recovery amounted to only 40%. As the polymerization observed during argon runs did not occur in the oxygen runs, it must be assumed that difficulties in the extraction of low molecular weight acids from the irradiated solutions were responsible for these poor material returns. All of the aldehydes afforded their corresponding carboxylic acids as the major product of irradiation, and lower molecular weight acids were formed as by-products. The carboxylic acids gave small yields of the lower molecular weight acids as their only irradiation products. Relative proportions of these products are given in Table VII.

Discussion

From the results on hand it is evident that two reaction pathways exist for aliphatic aldehydes under ultrasonic irradiation in water: oxidation to the corresponding carboxylic acid; and fragmentation to one- and two-carbon gases. For aliphatic carboxylic acids only the latter, less favored, pathway is available; hence, the acids are intrinsically more stable to ultrasonic irradiation. The points in need of clarification are the means and site of initiation for each process, and the probable intermediates of the fragmentation pathway.

Taking these in turn, we shall first consider the process of initiation for these reactions. Earlier work with the dialkyl sulfide[2] had suggested to us that an electron ejection might be the initial means by which some molecules become ultrasonically activated. In all probability this occurrence takes place at the surfaces of, or within the cavitation bubbles during their electrical discharge.[3] It seemed possible that aldehydes and carboxylic acids might fit the category of molecules activated in this fashion and accordingly we looked for

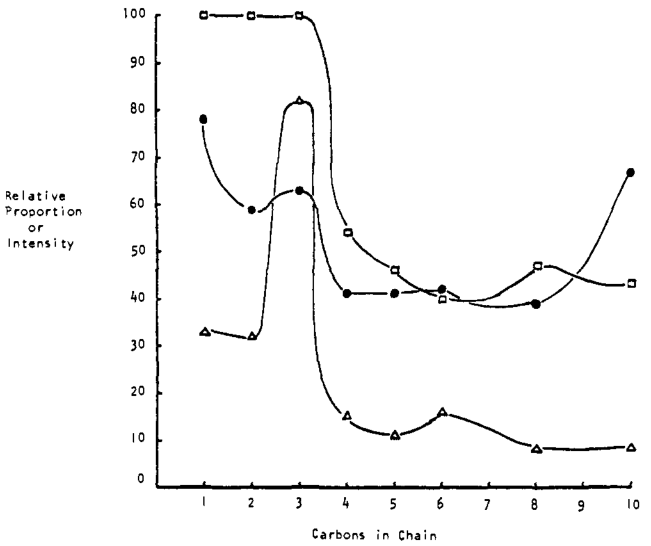

Figure 1. Comparison of carbon monoxide production through ultrasonic and mass spectral fragmentations of unbranched aliphatic aldehydes: (●) relative proportion of CO from ultrasonic reaction; (□) relative intensity of HCO^+ ion in mass spectrum; (△) relative intensity of CO^+ ion in mass spectrum.

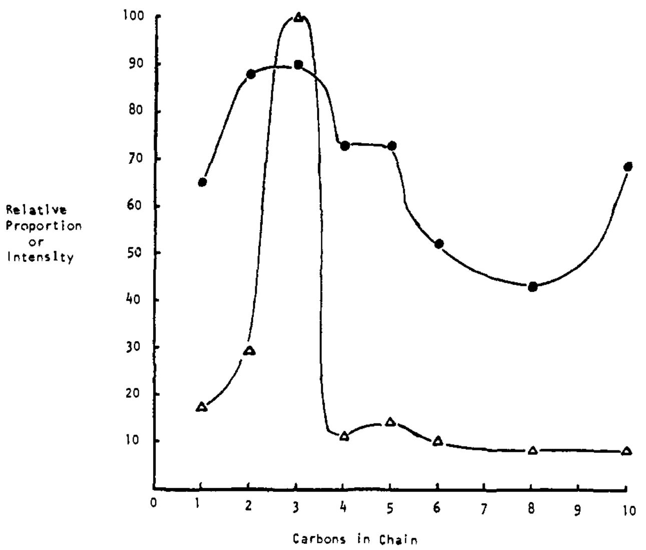

Figure 2. Comparison of carbon monoxide production through ultrasonic and mass spectral fragmentations of unbranched aliphatic carboxylic acids: ●, relative proportion of CO from ultrasonic reaction; △, relative intensity of CO^+ ion in mass spectrum.

similarities to other electron ejection reactions in an effort to substantiate this idea.

The simplest comparison, for which an abundance of appropriate experimental data already existed,[7] was with the fragmentations of ionized aldehydes and acids in a mass spectrometer. It appeared to us that the electron impact induced fragmentations of these species might lead to at least some similarities with ultrasonic fragmentations if the latter proceeded *via* the ionized parent molecules. The obvious drawbacks in this comparison are the uncertainty of ionizing energy available from the cavitation bubbles, and the abundance of secondary reaction pathways accessible to the initial ultrasonic fragments in solution which have no counterpart in the dilute gas phase of the mass spectrometer. It was for these reasons that we could only hope for a broad similarity in tendencies to give the fragments and, even then, only for the carbon monoxide and carbon dioxide products. The hydrocarbon products are more likely the results of multiple secondary reactions in solution than are these gases, and could hardly be expected to correlate with any primary process.

Figure 1 compares the tendencies of the aldehydes studied to give carbon monoxide during ultrasonic fragmentation, and the HCO^+ and CO^+ ions upon electron impact. (It is assumed that the HCO^+ ion which can be easily derived from an aldehyde, would be rapidly converted to carbon monoxide if formed in water by ultrasound.) The plot of carbon chain length *vs.* relative proportion of gaseous products, for ultrasound, and relative intensities of the ion peaks, for electron impact (70 eV), shows a general but irregular trend toward smaller proportions of these species with increasing chain length for ultrasonic and mass spectral processes. Interestingly, the small deviations in the trend for ultrasonic carbon monoxide proportion at propanal and hexanal are matched by similar deviations at the same aldehydes in the intensity of the CO^+ ion.

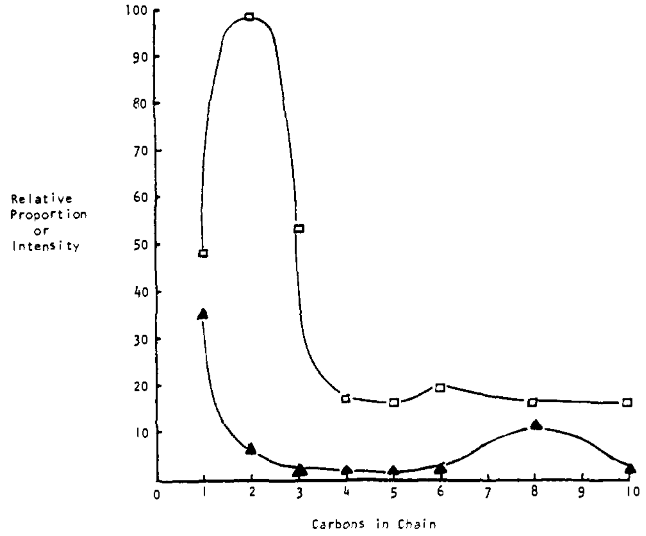

Figure 3. Comparison of carbon dioxide production through ultrasonic and mass spectral fragmentations of unbranched aliphatic carboxylic acids: ▲, relative proportion of CO_2 from ultrasonic reaction; □, relative intensity of CO_2H^+ ion in mass spectrum.

A similar comparative study of carbon monoxide production for the carboxylic acids is displayed in Figure 2. In this case a downward trend in proportion of the species being studied was not so pronounced. Nevertheless both ultrasonic carbon monoxide proportion and CO^+ ion intensity show similar variations as the chain length of the starting material increases, with a maximum proportion reached at propanoic acid. One may, in fact, speculate on whether this maximum is not also reflected in the propanal ultrasonic "deviation" mentioned earlier, since this aldehyde simultaneously undergoes efficient oxidation to the acid during ultrasonic irradiation.

In sonolyses of both aldehydes and acids the formation of carbon monoxide is a much more favorable process than formation of carbon dioxide. As is shown in Figure 3, where relative proportions of carbon dioxide from carboxylic acids are compared with relative

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(7) For example see J. A. Gilpin and F. W. McLafferty, *Anal. Chem.*, **29**, 990 (1957).

intensities of the CO_2H^+ ion, this is also essentially true of mass spectral fragmentations of carboxylic acids. In both modes of fragmentation the production of these species is only significant in the first few members of the homologous series.

These correlations notwithstanding, it is clear that ultrasonic fragmentation is specific for the functionality of the compound, and within the homologous series it is at least similar to the electron impact induced fragmentation process. Contrastingly, its rate is relatively insensitive to compound structure or functional group. (Note that the measured rates for all compounds, with the exception of methanoic acid, fall within a 12-fold rate span.) One may be tempted to conclude from these observations that the fragmentation is initiated by the electrical discharge within the cavitation bubble just prior to its collapse. Unfortunately, it is still not possible to totally rule out a thermolysis process as the energy source. A further case can nevertheless be made for reaction within the cavitation bubble if one remembers that the fragmentation pathway in an oxygen atmosphere leads to *no* gaseous products. Presumably, the reactive oxygen molecules can trap intermediates which, in an inert argon atmosphere, would be free to afford the gaseous fragments. This again suggests that fragmentation takes place in the gas phase, rather than in solution, and requires an energy source prior to the thermal gradient[8] generated by the collapse of the bubble.

In contrast to these observations on fragmentation, there is little reason to conclude that the simple oxidation of aldehydes to their corresponding carboxylic acids takes place at any site other than in solution. Deuterium labeling results, though equivocal, indicate that extensive hydrogen exchange takes place at the carbonyl carbon. Assuming that the abstraction of these hydrogens is accomplished by ultrasonically generated $\cdot$OH radicals in solution, it is reasonable that the resultant $R\dot{C}O$ radicals would be vulnerable to oxidation in the aqueous medium where more $\cdot$OH radicals are present. The initiation and termination of the oxidation process may therefore take place totally outside of the cavitation bubble.

The second of the originally mentioned points of clarification, the probable intermediates of fragmentation, is perhaps an even more complicated problem than detection of initiation sites. The results from deuterium studies suggest that the α carbon in carboxylic acids, and seemingly aldehydes, is vulnerable to abstraction, leading presumably to α radicals. It is alluring to conclude that these species may lead to fragmentation, especially if one considers them to be sources of α,β-unsaturated carbonyl compounds which should be more subject to oxidative carbon chain shortening. Indeed, a study of the gaseous products of probable intermediates in the fragmentation of propanoic acid (acrylic, lactic, and pyruvic acids) indicated that only the unsaturated acid, acrylic, could serve as a major intermediate. This was due to the similarity of its gaseous fragmentation products to those of the saturated acid, and the dissimilarity of the products from the others (see Table II). Additionally, gas chromatographs of the solution products from propanoic acid and all of the simple carboxylic acids with three carbons or more showed very minor amounts of materials with retention times identical to those of the corresponding α,β-unsaturated acids. Contradictorily, the deuterium labeled methane detected from D_2O experiments and, more important, from α,α-dideuteriobutanoic acid H_2O experiments indicates that a maximum of only one-half of the methane is derived from methyl radical attack on the solvent. The remainder seems to have been derived from hydrogen abstraction from the α carbon. This feat would be rendered highly improbable in the presence of an α radical. It is possible that these radicals play a role only in exchange and have no initial importance in fragmentation. Still, it must be remembered that a substantial retardation (38%) in the rate of gas evolution was discerned when the α,α-dideuteriobutanoic acid was irradiated. This isotope effect[9] clearly places some importance on the α-hydrogen removal process in the overall fragmentation reaction.

Once past the α radicals, little can be said with regard to intermediates except to indicate that any hydrocarbon other than propane and *n*-butane could have a transitory existence during the irradiations and serve as precursor for the observed gases. The long chain aldehydes and acids may in fact afford some long chain hydrocarbons as primary products, though none were detected despite attempts to do so.

A final comment is perhaps worth making in regard to the ultrasonic inertness of propane and *n*-butane as compared to the reactivity of *n*-pentane and *n*-hexane in aqueous suspension. The only rational explanation for this observation must lie in relative molecular sizes, since any argument based on physical state differences (or cavitation suppression) cannot explain the reactivities of propene and 1-butene. The ultrasonic degradation of these latter compounds could be facilitated by the ease of allylic hydrogen abstraction or the activation of the double bond. Either possibility correlates with the inertness of ethylene, which has no allylic hydrogens and has a higher ionization potential than propene or 1-butene.

Ultimately we must conclude that the reactions which we have studied are extremely complex processes with several reaction pathways proceeding simultaneously. It is evident that delineation of all of the concurrent reaction sequences is a thankless and nearly impossible job. We have, however, been able to deduce certain broad outlines in this work which should lay the ground work for our ultimate goal of greater predictability for ultrasonic reactions.

Experimental Section[10]

Irradiations of Aldehydes and Carboxylic Acids. The water for irradiation was purified by distillation from a concentrated aqueous

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[8] D. Srinivasan and L. V. Holyrod, *Phys. Rev.*, **99**, 633 (1955); V. Griffing and D. Setle, *ibid.*, 87, 234 (1952); M. E. Fitzgerald, V. Griffing, and I. Sullivan, *J. Chem. Phys.*, **25**, 926 (1956); V. Griffing, *ibid.*, 20, 939 (1952); M. Anbar and I. Pecht, *J. Phys. Chem.*, **68**, 1460, 1462 (1964).

[9] The enhanced rates of fragmentation in D_2O as compared to H_2O (see Table VI) are probably not a reflection of a simple isotope effect but, rather, result from enhanced cavitation effects in the denser D_2O medium.

[10] Irradiations were conducted with a Macrosonics Multisons 1100–broadband generator. Actual sound sources were cobalt barium titanate transducers, Model HFS-804, operating with maximum efficiency at 800 kHz with a rated average power output of 85 W, and lead zirconate titanate transducers, Models HFS-570 and HFS-250, operating with maximum efficiencies at 610 and 280 kHz, respectively, with rated average power outputs of 60 W. The irradiation vessel consisted of a cylindrical glass tube, 5 cm i.d. × 17 cm high, to which was affixed,

phosphoric acid solution. Before distillation, the system was purged with steam and then filled with an atmosphere of the appropriate gas. The water was then distilled directly into the reaction vessel. By this method water was obtained at pH 7. To 300 ml of water purified in this fashion was added enough material for irradiation to bring the suspension or solution to 0.006 *M*. A positive flow of the saturating gas was maintained during the addition of the organic compound in order to avoid simultaneous admission of air to the apparatus. For runs in D_2O,[11] argon gas was bubbled through the D_2O in the reaction vessel for 1 hr, displacing dissolved air, prior to addition of the butanoic acid or butanal. In all runs the gaseous products were analyzed by gas chromatography. Two columns were used. Carbon dioxide and methane were analyzed on a 10 ft × $^1/_8$ in. molecular sieve column operated at ambient temperature with a 10-ml per hr nitrogen flow rate. A 12 ft × $^1/_8$ in. Porapak R column, operated at ambient temperature with a 15-ml per hr nitrogen flow, was used to analyze carbon monoxide, methane, ethane, ethylene, and acetylene. The rate of gas evolution during irradiation was followed using a gas buret. The aqueous phase in the irradiated reaction vessel was analyzed by saturating the solutions with sodium chloride and continuous extraction with diethyl ether for 16 hr. After evaporation of the ether the residues were analyzed by gas chromatography. The column utilized was a 10 ft × $^1/_8$ in. 30% DEHS operated at 150° with a 30-ml/hr helium flow rate. To examine the deuterium label in the methane product, gas samples were removed from above the irradiated solutions with a gas syringe. These samples were then admitted to the mass spectrometer and spectra taken utilizing a 25-eV chamber voltage. Butanoic acid and butanal recovered from D_2O runs by conventional extraction techniques were also analyzed by mass spectrometry (chamber voltage employed was 25 eV). A similar analytical procedure was employed for runs with α,α-dideuteriobutanoic acid.[12]

Irradiations of Hydrocarbons. In the cases of gaseous hydrocarbons, 70 ml of the gas was bubbled into 300 ml of water purified as in the previously described cases under argon. The mixture was then irradiated for 3 hr under conditions identical with those utilized for the aldehydes and acids. The liquid hydrocarbons were added as 100-mg samples to the water–argon and irradiated similarly.

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at the lower end, a disk of 500 D Mylar film serving as the sound-transparent bottom, and, at the upper end, gas inlet and outlet fixtures for control of the internal gaseous atmosphere. The vessel was fitted to an external cooling jacket by means of standard ground-glass joints which also served to maintain a reproducible distance between the surface of the transducer and the bottom of the vessel (approximately 1 cm). Sound coupling between source and vessel occurred through the water in circulation through the cooling jacket. Relative intensity measurements were made with a Macrosonics cavitation meter, Model CVM-3a. Actual intensity was estimated from the rated average output of the transducers at maximum efficiency. Infrared analyses were effected with a Perkin-Elmer Model 237B grating infrared spectrophotometer, and gc analyses accomplished with a Perkin-Elmer G-11 gas chromatograph with hot-wire detector and linear temperature programmer. A Perkin-Elmer Hitachi RMU 6 mass spectrometer was operated with a chamber voltage of 25 eV. All aldehydes and acids were purchased from Aldrich Chemical Co. All compounds were purified by distillation under an argon atmosphere with the exception of decanal and decanoic acid, which were recrystallized from hexane in a Dry Ice–acetone bath.

(11) The D_2O was 99% deuterated and was used as purchased from Stohler Isotope Chemicals.

(12) We wish to thank Dr. Terry E. Parks for his donation of the sample of α,α-dideuteriobutanoic acid which was used for these studies. A mass spectrum of this material showed it to be 95% dideuterated.

Virial Partitioning of Charge Distributions and Properties of Diatomic Hydrides

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Abstract: A spatial partitioning of the molecular charge distributions and energies of diatomic hydrides is presented. The partitioning surface is defined by the path of the gradient vector of $\rho(\mathbf{x})$, passing through the point of minimum density between the nuclei. The kinetic and potential energies of molecular fragments determined by such a surface are well defined and, in addition, satisfy the quantum mechanical virial relationship. The virial partitioning method divides a total system into subsystems, each of which is quantum mechanically self-contained. This feature is further evidenced in the observation that the constancy in the properties of a bonded fragment in different systems is reflected in the constancy of both its charge distribution *and* virial. The virial partitioning method is applied to diatomic hydrides ($HeH^+ \rightarrow HF$), neutral and charged, in their ground and excited states to yield fragment populations, kinetic and potential energies. The origin and type of binding in ground-state AH systems is described in terms of this partitioning procedure. A quantitative proposal is made, in answer to the question "are there atoms in molecules?"

In this paper we apply and illustrate an objective and fundamental partitioning procedure to properties of diatomic hydride molecules. The partitioning procedure is objective since it is unambiguously determined by the topological properties of the molecular charge distribution. It is fundamental since it yields values for the kinetic and potential energies of the fragments which are not only well defined, but satisfy the quantum-mechanical virial theorem. Thus, the *virial partitioning method* yields fragments whose average energies obey the same quantum-mechanical relationship as do the average energies of the total system.[1,2]

The fragments defined by the virial partitioning method account for one of the most important observations in chemistry: retention of the identity and properties of bonded fragments in different systems, a retention which in many instances is so close as to give rise to bond additivity schemes for the energy. The extent to which properties are additive between different systems is determined by the extent to which the charge distribu-

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(2) R. F. W. Bader, P. M. Beddall, and J. Peslak, Jr., *ibid.*, submitted for publication.