COMMUNICATION

ChemComm
www.rsc.org/chemcomm

The role of solvent in sonochemical reactions: the case of acetic acid

Takahide Kimura,*[a] Hisashi Harada,[b] Takashi Ando,[a] Mitsue Fujita,[a] Jean-Marc Levêque[c] and Jean-Louis Luche[c]
[a] *Department of Chemistry, Shiga University of Medical Science, Seta, Otsu, Shiga 520-2192, Japan.*
E-mail: kimura@belle.shiga-med.ac.jp; Fax: +81-77-548-2102; Tel: +81-77-548-2102
[b] *Department of Chemistry, Faculty of Physical Sciences and Engineering, Meisei University, Hodokubo,*
Hino, Tokyo 191-8506, Japan. E-mail: harada@chem.meisei-u.ac.jp; Fax: +81-42-591-8181;
Tel: +81-42-591-7462
[c] *Laboratoire de Chimie Moléculaire et Environnement, Université de Savoie, F-73376 Le Bourget du Lac*
Cedex, France. E-mail: jean-louis.luche@univ-savoie.fr; Fax: +33 479 75 88 85; Tel: +33 479 75 88 59

Received (in Cambridge, UK) 6th March 2002, Accepted 9th April 2002
First published as an Advance Article on the web 29th April 2002

Among the sonolysis products of acetic acid, oxidizing intermediates can play a direct role in reactions run in this solvent, illustrating the fact that organic sonochemistry can originate in organic solvents as aqueous sonochemistry can in water.

The admitted origin of sonochemistry in aqueous solutions is water sonolysis, which generates the radicals inducing the subsequent reactions.[1] Contrastingly in organic solutions the mechanism remain imprecise: if vaporization into the cavitation bubbles explains the fate of volatile molecules, this phenomenon seems unlikely for non-volatile or solvated substrates. A relay mechanism involving solvent-derived species offers a possibility worthy of consideration. Confirmation of this hypothesis would provide a unified view on sonochemistry, by establishing that *organic sonochemistry originates in organic solvents as aqueous sonochemistry originates in water*. However, except for a few alkanes, lower-weight alcohols, formamide, toluene,[2] the sonochemistry of most solvents is not known. Our first step towards a demonstration of the statement is concerned with acetic acid, in continuation of our previous work on the lead tetraacetate–4-substituted styrene (4-X-Sty) reactions.[3] A linear free energy relationship was found between the reactivities of the substrates, their vapor pressure,[4] and the amount of the radical-cation $[\text{4-X-Sty}]^{+\cdot}$ formed in the cavities.[5] Direct activation of styrene is, however, unlikely since its pyrolysis or shock wave decomposition, both resulting from the bubble collapse,[2,6] yields benzene and acetylene *via* a non-radical process,[7] and acetic acid is > 300 times more abundant, and volatile ($v_{\text{p }25\ °\text{C}}$: 15.4 mmHg), than styrene (v_p: 6.3 mmHg). If the bubble contains mostly AcOH, its sonolysis is much more probable than that of styrene, and $[\text{4-X-Sty}]^{+\cdot}$ can result from reaction(s) of the parent olefin with oxidizers generated from the solvent, an hypothesis in line with some unexplained literature data.[8]

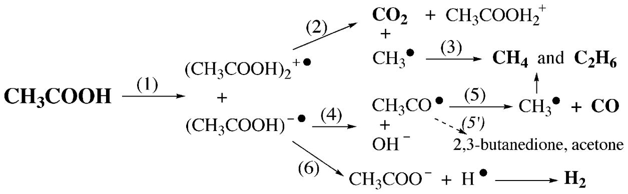
The sonolysis of acetic acid was performed by submitting a 30 mL sample (99.7%), pure or with dissolved potassium acetate (0.82 M) to a 200 kHz continuous wave (*ca.* 5 W)[9] at 25 °C under Ar, in a thermostated pear-shaped cell (300 mL). The gaseous products were analyzed by VPC (TC detection). All the experiments were conducted at least twice, with an accuracy estimated to ± 6%.

The tables below give the relative amounts of the gases after 6 h and their formation rates.

These results show that in all the cases, the overall rate of gas evolution is smaller than that of hydrogen from pure water, but only by a factor of 4–5. This can reflect the lower cavitation energy released by acetic acid.[10] Carbon monoxide, the most abundant gas, represents more than one third of the total. Methane and carbon dioxide are produced in similar amounts and rates. Potassium acetate accelerates the gas formation, but this effect is not the same for all the effluents. The increase reaches *ca.* 70% for H_2, CH_4, and CO_2, but CO is much less affected. Water has an opposite but limited effect, which means that: (i) as no increase in the hydrogen percentage is noted, its sonolysis should not be significant, and (ii) its presence in small amounts due to an imperfect drying of the samples should be of little consequence.

The interpretation of these data can be based on two physical effects of the cavitational collapse, the radiomimetic effect, and the shock wave emission, which relate sonolysis to γ-radiolysis, and to shock tube thermolysis, respectively.

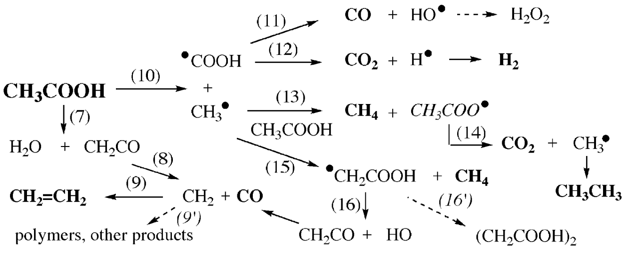
γ-Radiolysis (Scheme 1) starts with a radiation-induced electron exchange between 3 molecules of AcOH,[11] then the radical-ion pair decomposes as in reactions (2)–(6). The $CH_3^{\cdot}$ radicals abstract hydrogen from any donor present in the medium to give methane, or dimerize to ethane but this diffusion limited process is less favoured. The radical-anion cleaves (4) to $CH_3CO^{\cdot}$, further decomposed to CO and $CH_3^{\cdot}$ (5), or to acetate and a hydrogen atom (6).



Scheme 1 Radiolysis of acetic acid.

A qualitative analogy seems thus to exist with sonolysis, since most gaseous species found in the sonochemical experiments are present in this scheme except ethene. However, the oxidizing properties of the sonicated medium are not easily explained, leading to envisage a better approach.

The reactions induced by shock wave (Scheme 2) can follow non-radical and radical pathways. The first one predominates,[12] and starts with the dehydration of acetic acid to ketene (7), a reaction also favoured under thermolysis.[13] Cleavage to CO and carbene occurs, followed by the formation of ethene and probably other products. The high percentages of CO (Table 1 and 2) confirms that this pathway should also be followed under sonication. The much lower amounts of ethene determined in the shock wave and the sonochemical experiments as well, can be explained by the fast reactions of carbene with the solvent or its polymerization.



Scheme 2 Shock wave cleavage of acetic acid

DOI: 10.1039/b202350d

Table 1 Average composition of the gas phase at 6 h reaction time

	Sonication medium	Relative gas amounts (%)						Total gas evolved/μmol
		H_2	CH_4	CO_2	C_2H_4	C_2H_6	CO	
1	Pure AcOH	12 ± 2	17 ± 2	16 ± 3	6 ± 2	5 ± 2	44 ± 7	23 ± 3
2	AcOH + AcOK (0.82 M)	16 ± 3	20 ± 5	20 ± 3	4 ± 1	5 ± 2	34 ± 9	32 ± 5
3	AcOH + AcOK (0.82 M) + 1% H_2O	16 ± 2	20 ± 3	19 ± 3	6 ± 2	6 ± 2	34 ± 5	29 ± 3

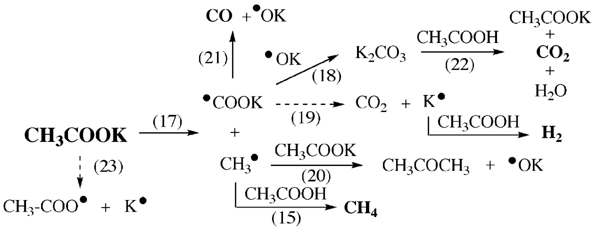
Table 2 Rates of the gas evolution

	Sonication medium	Rates ($\times 10^{-7}$ mol h^{-1} at 25 °C)						
		H_2	CH_4	CO_2	C_2H_4	C_2H_6	CO	Total
1	Pure AcOH	4.9	6.5	6.1	2.1	2.1	16.8	38.5
2	AcOH + AcOK (0.82 M)	8.2	11.1	10.6	2.5	2.9	19.2	54.4
	% increase[a]	*67*	*71*	*74*	*19*	*38*	*14*	*40*
3	AcOH + AcOK (0.82 M) + 1% H_2O	7.4	9.4	8.6	2.9	2.9	16.4	47.5
	% increase[b]	*−10*	*−15*	*−19*	*16*	*0*	*−14*	*−13*
4	Pure H_2O	*ca.* 200						

[a] Between entries 1 and 2. [b] Between entries 2 and 3.

Among the more important radical processes,[12] reactions (10) and (13) account for the formations of CO_2, H_2, and CH_4, with (13) involving the acetyloxy radical as a transient intermediate. This species is probably responsible for the oxidizing properties of sonicated acetic acid,[4,5,8] and despite its short lifetime, it was shown to be able to add to olefins.[14]

The role of potassium acetate is visualized in Scheme 3.



Scheme 3 Decomposition of potassium acetate

The thermal decomposition of alkali and alkali-earth carboxylates *via* a chain mechanism was once used for the synthesis of carbonyl compounds.[15] The process starts with the homolysis (17) of the salt. As its pyrolysis appears to be easier than that of the acid itself, we can logically deduce that reaction (17) is faster than (10) (Scheme 2), and can occur either in the heated bubble shell or at its proximity under the effect of the shock waves. The higher rates for the formations of hydrogen, CH_4, and CO_2 can be explained by the acceleration of this first step, while the less probable cleavage (21) leaves the formation of CO much less affected. Similarly, the formations of ethane and ethene implying a dimerization step occur less readily in a more viscous solution. The recombination reaction (18) yields potassium carbonate. In the acidic solution, potassium acetate is regenerated (22), explaining its catalytic role.

The initial decomposition of potassium acetate can also occur *via* reaction (23). In support to this assumption, Lepoint *et al.* have shown that ‘alkali metal salts released into a bubble undergo a homolytic cleavage so as to generate alkali metal atoms’.[16]

The importance of shock wave effects in the sonochemistry of solutions is underlined here, and confirmation of these interpretations will be searched with the necessary (but technically difficult) analysis of the liquid phases. Nevertheless, at this stage, the formation of an oxidizer in these solutions is highly probable, which supports the initial hypothesis that in sonochemical reactions, the role of the solvent is not only that of an energy carrier, but it can also act as an active chemical relay. This conclusion appears especially important to rationalize sonochemical reactions between solutes less volatile than the solvent. This situation recognized a long time ago for water and aqueous solutions, seems to have been overlooked for organic media.

The present work was supported by a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology. This work was done as a part of a European Cooperation Programme (COST D10/0008).

Notes and references

1 For a recent review, see *inter alia*: C. Pétrier and D. Casadonte, *Adv. Sonochem.*, 2001, **6**, 91.
2 Y. Mizukoshi, H. Nakamura, H. Bandow, Y. Maeda and Y. Nagata, *Ultrason. Sonochem.*, 1999, **6**, 203; V. Misik and P. Riesz, *J. Phys. Chem.*, 1994, **98**, 1634; K. S. Suslick, J. J. Gawienowski, P. F. Schubert and H. H. Wang, *Ultrasonics*, 1984, **22**, 33.
3 T. Ando, T. Kimura, J.-M. Levêque, J.-P. Lorimer, J.-L. Luche and T. J. Mason, *J. Org. Chem.*, 1998, **63**, 9561, and refs. cited therein.
4 T. Ando, T. Kimura, J.-M. Levêque, M. Fujita and J.-L. Luche, *Chem. Lett.*, 2000, 1124.
5 T. Ando, T. Kimura, M. Fujita, J.-M. Levêque and J.-L. Luche, *Tetrahedron Lett.*, 2001, **42**, 6865.
6 Cavitation induced shock waves can reach 39–500 kbar. K. Weninger, P. Evans, S. Putterman, and G. Vasquez, *2000, International Chemical Congress of Pacific Basin Societies*, Honolulu, Hawaii, Dec. 14-19, 2000, Abstract 1464.
7 M. A. Grela, V. T. Amorebieta and A. J. Colussi, *J. Phys. Chem.*, 1992, **96**, 9861.
8 M. Allegretti, A. D′Annibale and C. Trogolo, *Tetrahedron*, 1993, **49**, 10705.
9 T. Kimura, T. Sakamoto, J.-M. Lévêque, H. Sohmiya, M. Fujita, S. Ikeda and T. Ando, *Ultrason. Sonochem.*, 1996, **3**, 157.
10 B. Niemczewski, *Ultrasonics*, 1980, S107.
11 V. N. Belevskii and S. I. Belopushkin, *High Energy Chem.*, 1991, **25**, 342.
12 K. R. Doolan, J. C. Mackie and C. R. Reid, *Int. J. Chem. Kinet.*, 1986, **18**, 575.
13 K. Saito, T. Sasaki, I. Yoshinobu and A. Imamura, *Chem. Phys. Lett.*, 1990, **170**, 385; P. Ruelle, *Chem. Phys.*, 1986, **110**, 263.
14 J. C. Martin, J. W. Taylor and E. H. Drew, *J. Am. Chem. Soc.*, 1967, **89**, 129.
15 M. Zielinski, in *The Chemistry of Carboxylic Acids and Esters*, ed. S. Patai, Interscience, John Wiley, London, 1969, pp. 453.
16 F. Lepoint-Mullie, N. Voglet, T. Lepoint and R. Avni, *Ultrason. Sonochem.*, 2001, **8**, 151See also: E. B. Flint and K. S. Suslick, *J. Phys. Chem.*, 1991, **95**, 1484.