S0032-3861(96)00197-8

Polymer Vol. 37 No. 17, pp. 3971-3973, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

polymer communications

Sonochemical acceleration of persulfate decomposition

Gareth J. Price* and Andrew A. Clifton
School of Chemistry, University of Bath, Bath BA2 7AY, UK
(Received 3 January 1996)

The decomposition kinetics of potassium persulfate in aqueous solution have been investigated using a radical trapping method. The use of ultrasound was found to markedly accelerate the decomposition so that the sonochemical process at 25°C occurs at the same rate as the purely thermal reaction at 55°C. The effect of ultrasound intensity has also been studied and can be used to control the rate of decomposition within certain limits. Copyright © 1996 Elsevier Science Ltd.

(Keywords: sonochemistry; persulfate; radical initiation)

Introduction

Metal persulfates are commonly used sources of radicals in aqueous solutions. For example the potassium and ammonium salts are used to initiate polymerization in aqueous and emulsion systems and also as relatively mild oxidizing agents[1,2]. The mechanism of the thermal decomposition is believed[3] to involve the sulfate radical which can abstract a hydrogen from water to give hydroxyl radicals.

$$S_2O_8^{2-} \rightarrow 2\ SO_4^{\dot{-}}$$

$$2\ SO_4^{\dot{-}} + H_2O \rightarrow HSO_4^- + HO^{\bullet}$$

Either of the radical species can, in principle, act as an initiator. However, the decomposition has a relatively high activation energy[4,5] of around 130 kJ mol^{-1} and so is relatively slow at room temperature and acceptable rates can only be achieved above 50°C. Production of radicals can also be accelerated by traces of metal salts[6] such as Ag, Fe and Cu.

Over the past two decades, the use of high intensity ultrasound has become a common technique in synthetic chemistry[6-8] leading to a branch of chemistry sometimes termed *sonochemistry*. Although most commonly used in heterogeneous systems, a number of homogeneous reactions[10-12] have also been shown to give enhanced rates and yields under ultrasound. The best known effect in polymer sonochemistry is the cleavage of chains when irradiated in solution[13,14] although more recently, ultrasound has been applied to polymer synthesis with some success[15] including emulsion systems[16,17].

The main effects of sonication are due to *cavitation* or the growth and explosive collapse of microscopic bubbles on a microsecond timescale[18]. This can result in the formation of relatively high concentrations of radicals due to breakdown of solvent but can also accelerate the decomposition of compounds such as AIBN or benzoyl peroxide[19-21]. Calculations[18] show that conditions inside the collapsing bubbles simulate very high temperatures (> 2000 K) and pressures (> 500 bar) resulting in the breakdown of solvent. Reactions in solution can also be enhanced as a result of increased local temperatures in the vicinity of a bubble or by combination with sonochemically generated intermediates. An additional factor to be considered is that sonochemical reactions are often more efficient at low temperature because the solvent has a lower vapour pressure and higher viscosity so that cavitation is intensified.

In a very early report, Schumb and Ritner[22] showed that the rate of decomposition of potassium persulfate was increased by ~ 10% during sonication at 8.7 kHz, although no details of ultrasound conditions were quoted. More recently, Lorimer *et al.*[23] reported an increase in the rate of decomposition between 50 and 80°C, although lower temperatures were not studied. Their work utilized a polarographic method for determining the amount of persulfate remaining. We have used an alternative method involving trapping the generated radicals in order to monitor their rate of production. In aqueous solution, a suitable trap is N-*t*-butyl-α-phenyl nitrone, TBPN. This method has been widely and successfully used in sonochemical and other systems by a number of workers including Riesz[24,25] and Sridhar *et al.*[26]. The work showed that the rate of addition of radicals to TBPN is extremely rapid in comparison to the rate of radical production so that meaningful measurements of the latter can be made.

In connection with other work, we were interested in using persulfates as oxidizing agents at room temperature. Also, it was of interest to determine whether ultrasound could allow the use of persulfates to initiate polymerization at low temperature in a controlled manner. This communication therefore briefly describes the measurement of the decomposition kinetics for potassium persulfate at several temperatures and ultrasonic intensities.

Experimental

Materials. The N-*t*-butyl-α-phenyl nitrone, TBPN, was obtained from Sigma. All other reagents and solvents were of the purest grade available from Aldrich Ltd. The water used to prepare the solutions was distilled and purified by ion-exchange.

Sonication procedures. Solutions were contained in a

---

* To whom correspondence should be addressed

250 cm^3 jacketted beaker. Thermostatted water was circulated to maintain temperature control to ±0.5°C. A 'Sonics and Materials' VC600 ultrasound horn system was fitted so that the horn tip was ~2 cm below the surface of the solution. The intensity of ultrasound, measured calorimetrically[27] was $26.2 \pm 1.5\,\mathrm{W\,cm^{-2}}$. Blank experiments were carried out in the same apparatus without switching on the ultrasound but with magnetic stirring.

150 cm^3 of purified water was placed in the beaker and allowed to reach the required temperature. 0.15 g (5.5×10^{-4} mol) of potassium persulfate and a two-fold excess of TBPN were added and stirred rapidly until dissolved. A cover was fitted to the beaker and, for the sonochemical runs, the sonicator switched on. Periodically, 0.20 cm^3 of the solution was removed using a syringe and diluted to 25.0 cm^3 with cold water to quench the reaction before being analysed on a Perkin Elmer PE330) u.v. spectrometer. TBPN has a characteristic absorbance at 287 nm which is removed on reaction with a radical.

Results and discussion

The rate plots for the consumption of TBPN for the thermal and sonochemical reactions are shown in *Figures 1* and *2* respectively. As previously reported, the processes were first order, confirming that the production of radicals was the rate-limiting step. Rate constants were calculated in the usual manner and are shown in *Table 1*. It can be seen that the rates were comparable for both processes at ~65°C but that the sonochemical rates were significantly faster at low temperatures. There was at least a ten-fold increase in the rate constant for radical production around room temperature. It is well known that hydroxyl radicals can be produced by the ultrasonic fragmentation of water[24,28]. However, under the conditions used here, the rates are much lower than those measured here and should be negligible (< 0.5%) in comparison[29]. Above 65°C, there was no benefit in using ultrasound and the rate was slower than that observed for the thermal process alone. While cavitation will be much reduced at higher temperatures due to the relatively high vapour pressure of the water, the reasons for the reduction in rate are not totally clear but may be due in part to less efficient mixing in the sonochemical reactions where no additional extra stirring was used.

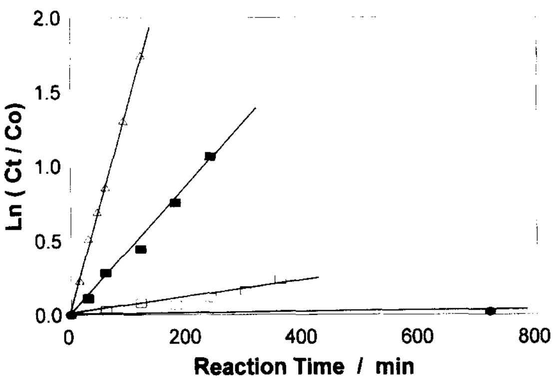

Figure 1 Rate plot for the consumption of TBPN by the thermal decomposition of potassium persulfate. Temperature/°C: △, 75; ■, 65; □, 55; ●, 35

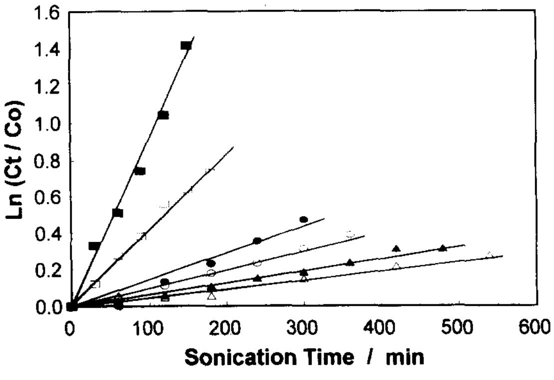

Figure 2 Rate plot for the consumption of TBPN by the sonochemical decomposition of potassium persulfate. Temperature/°C: ■, 75; □, 65; ●, 55; ○, 45; ▲, 35; △, 25

An Arrhenius plot of the results is shown in *Figure 3*. The thermal process yielded a value for the activation energy of $121 \pm 12\,\mathrm{kJ\,mol^{-1}}$ which is in reasonable agreement with previous work[4,33]. The plot for the sonochemical decomposition is non-linear and the apparent activation energy becomes lower as the temperature is reduced. A number of sonochemical processes have been found to occur with negative apparent activation energies as a consequence of cavitation being more efficient at low temperatures. If it is assumed that two concurrent processes take place, the conventional, thermal reaction with a rate constant k_{th} and the ultrasonic process with a rate k_{us}, then the observed rate constant, k_{obs} will be given by

$$k_{\mathrm{obs}} = k_{\mathrm{th}} + k_{\mathrm{us}}$$

Also shown in *Figure 3* is the Arrhenius plot for solely the sonochemical process. The slope is opposite to that for the overall rate constant and gives an apparent activation

Table 1 First order rate constants for potassium persulfate decomposition

Temperature (°C)	Rate constant (10^3 min^{-1}) Thermal	Sonochemical
25		0.51
35	0.07	0.70
45		1.09
55	0.59	1.67
65	4.37	4.18
75	14.3	8.99

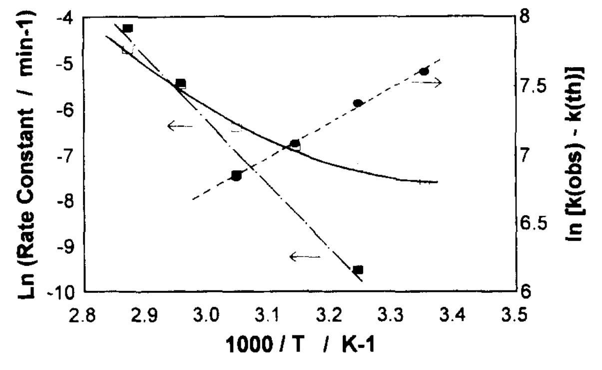

Figure 3 Arrhenius plot for the decomposition of potassium persulfate. ■, Absence of ultrasound; □, presence of ultrasound; ●, difference between presence (k_{obs}) and absence (k_{th})

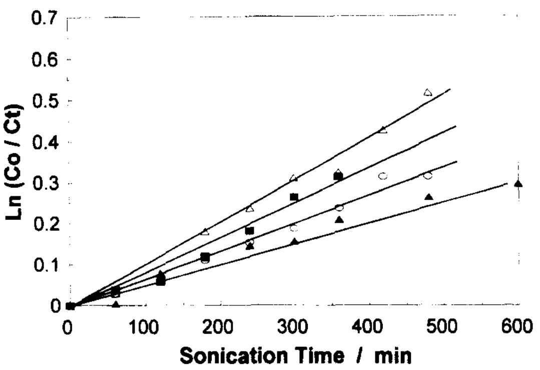

Figure 4 Rate plot for the consumption of TBPN by the thermal decomposition of potassium persulfate at 35°C. Ultrasound intensity/ W cm^{-2}: △, 33.2; ■, 49.1; ○, 26.2; ▲, 16.8

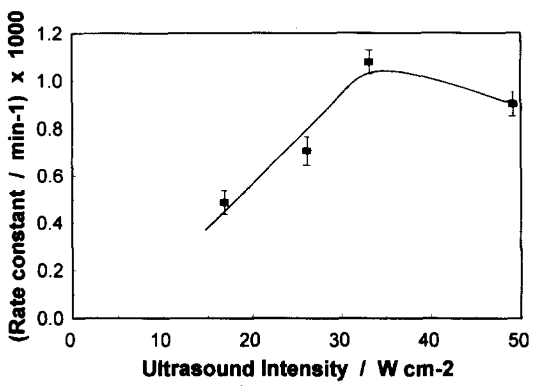

Figure 5 Rate constants (min^{-1}) for the decomposition of potassium persulfate at 35°C as a function of ultrasound intensity

energy of −21.1 kJ mol^{-1}. The term 'apparent' is used since the physical meaning of a negative activation energy is uncertain. This value is similar to that for radical production in methyl methacrylate measured using a similar technique[19].

Figure 4 shows the rate of consumption of TBPN as a function of the ultrasonic intensity at a constant temperature of 35°C. As expected, the rate increased at higher intensities although the effect was much smaller than that of varying the temperature. As shown in *Figure 5*, the rate constant passed through a maximum value at ~ 33 W cm^{-2}. This feature has been noted[30] by several workers for a range of reactions. While a complete explanation remains unclear, the effect can in part be attributed to an increase in the intensity increasing both the number and size of the cavitation bubbles. The size increase cannot continue indefinitely since they may become too large to collapse during the compression cycle of the cavitation process[31]. In addition, the transmission of sound through the liquid may be perturbed by the large bubble field making cavitation less efficient.

Conclusion

This work has shown that ultrasound can be used to significantly accelerate the decomposition of potassium persulfate. The sonochemical process at 25°C occurs at the same rate as the purely thermal reaction at 55°C so that the use of persulfates for initiation or oxidation around room temperatures becomes viable. Reasonable control over the rates can be gained by varying the temperature or intensity although there is an optimum value of the ultrasound intensity above which no further benefit can be gained.

Acknowledgement

We are grateful to EPSRC for the award of a research studentship (to AAC) and to BICC Ltd. for additional funding of this work.

References

1 Shalaby, S. W., McCormick, C. L. and Butler, G. B. (Eds) 'Water Soluble Polymers', A.C.S. Symposium Series 467, A.C.S., Washington, 1991
2 Bamford, C. H. in 'Comprehensive Polymer Science' (Eds G. Allen and J. C. Bevington) Vol. 3, Ch. 9, Pergamon, Oxford, 1989
3 Bartlett, P. D. and Colman, J. D. *J. Am. Chem. Soc.* 1949, **71**, 1419
4 Rasmussen, J. K., Heidmann, S. M., Torn, P. E., Pocius, A. V. and Kotnar, T. A. *J. Am. Chem. Soc.* 1983, **105**, 6849
5 Kolthoff, I. M. and Miller, I. K. *J. Am. Chem. Soc.* 1951, **73**, 3055
6 Anderson, J. M. and Kochi, J. K. *J. Am. Chem. Soc.* 1970, **92**, 1651
7 Suslick, K. S. 'Ultrasound: Its Chemical, Physical and Biological Effects', Chapter 4, VCH Publishers, New York, 1990
8 Ley, S. V. and Low, C. R. 'Ultrasound in Chemistry', Springer Verlag, London, 1989
9 Price, G. J. (Ed.) 'Current Trends in Sonochemistry', RSC Special Publication **116**, RSC, Cambridge, 1992
10 Suslick, K. S. Reference 7, Chapter 4
11 Yu, T. J., Sutherland, R. G. and Varrall, R. E. *Can. J. Chem.* 1980, **58**, 1909
12 Broeckart, L., Caulier, T., Fabre, O., Maerschalk, C., Reisse, J., Vandercammen, J., Yang, D., Lepoint, T. and Mullie, F. Reference 9, Chapter 2
13 Basedow, A. M. and Ebert, K. *Adv. Polym. Sci.* 1997, **22**, 83
14 Price, G. J. *Adv. Sonochem.* 1990, **1**, 231
15 Price, G. J. 'New Methods of Polymer Synthesis' (Eds J. R. Ebdon and G. C. Eastmond), Vol. 2, Ch. 4, Blackie, Glasgow, 1995
16 Biggs, S. and Grieser, F. *Macromolecules* 1995, **28**, 4877
17 Chou, H. C., Lin, W. Y. and Stoffer, J. O. *Polym. Mater. Sci. Eng.* 1995, **72**, 363
18 Leighton, T. 'The Acoustic Bubble', Academic Press, London, 1994
19 Price, G. J., Norris, D. J. and West, P. J. *Macromolecules* 1992, **25**, 6447
20 Orszulik, S. T. *Polymer* 1993, **34**, 1320
21 Lorimer, J. P., Mason, T. J. and Kershaw, D. *J. Chem. Soc. Chem. Commun.* 1991, 1217
22 Schumb, W. C. and Rittner, E. S. *J. Am. Chem. Soc.* 1940, **62**, 3416
23 Lorimer, J. P., Mason, T. J., Fiddy, K., Groves, R. and Dodgson, D. 'Ultrasonics International Conference Proceedings', 1989, 1283
24 Riesz, P. *Adv. Sonochemistry* 1992, **2**, 23
25 Makino, K., Mossoba, M. M. and Reisz, P. *J. Phys. Chem.* 1983, **87**, 1369
26 Sridhar, R., Beaumont, P. C. and Powers E. L. *J. Radioanal. Nuclear Chem.* 1986, **101**, 227
27 Mason, T. J. 'Practical Sonochemistry', Ellis Horwood, Chichester, 1991
28 Petrier, C., Jeunet, A., Luche, J-L. and Reverdy, G. *J. Am. Chem. Soc.* 1992, **114**, 3149
29 Price, G. J. and Lenz, E. J. *Ultrasonics* 1993, **31**, 451
30 Gutierrez, M. and Henglein, A. *J. Phys. Chem.* 1990, **94**, 3625
31 Neppiras, E. A. and Notlingk, B. E. *Proc. Roy. Soc.* 1950, **B63**, 1032