Dimerization of α-Methylstyrene (AMS): Kinetic Study of the Liquid–Liquid Process

Bhaswati Ghosh and Basab Chaudhuri
Dept. of Chemical Engineering, University of Calcutta, Calcutta 700091, India

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The dimerization of α-methylstyrene (AMS) in the presence of aqueous sulfuric acid catalyst in liquid–liquid (L–L) mode of operation has been studied and the kinetic parameters have been determined. There was no mass transfer limitation in the process and the reaction was found to be intrinsically first-order. The rate constants, activation energy, and product distribution for the L–L mode of operation have been reported. A plausible explanation for the formation of the industrially important dimer in the presence of alcohols has been presented. The data are new and have not been previously reported in the literature. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1847–1854, 2006
Keywords: α-methylstyrene, dimerization, liquid-liquid, acid-catalyzed, kinetics

Introduction

The acid-catalyzed dimerization of α-methylstyrene (AMS) is an organic reaction of commercial importance and academic interest. In the acid-catalyzed dimerization of AMS, a number of products are formed. These products include 2,4-diphenyl-4-methyl-1-pentene (UD1), 2,4-diphenyl-4-methyl-2-pentene (UD2), and 1,1,3-trimethyl-3-phenylindan, also called saturated dimer (SD). Under certain conditions, one more saturated dimer, *cis*- and/or *trans*-1,3-dimethyl-1,3-diphenylcyclobutane (CB) may also be formed. Scheme 1 gives the products obtained from the dimerization of AMS.

The unsaturated dimers of AMS are useful as chain-transfer agents or molecular weight regulators in the production of polymers such as polystyrene, SAN [poly(styrene-*co*-acrylonitrile)] resin, ABS (acrylonitrile–butadiene–styrene) resin, SBR (styrene butadiene rubber), and the like. Of the unsaturated dimers, UD2 is not preferred as a molecular weight regulator because it hinders the initiating reaction and accordingly requires an undesirably longer induction period. Furthermore, the saturated indanic dimer SD and higher oligomers (such as trimers and tetramers) are of no value as molecular weight regulators, and their presence in the product dimer unnecessarily reduces the effective concentration of UD1. So that the unsaturated dimers of AMS can function effectively as molecular weight regulators, the purity of UD1 in the product dimer should be as high as possible, preferably $>$93%.

To date, the most extensive study on the dimerization of AMS is that reported by Chaudhuri and Sharma,[1] who described a method of commercially producing UD1 of purity $>$ 92% by conducting the dimerization in the presence of solid acid catalysts such as ion-exchange resins under carefully controlled conditions and also with aqueous sulfuric acid as a catalyst in a heterogeneous liquid–liquid (L–L) system. The problem with the heterogeneous L–L system with aqueous sulfuric acid as a catalyst was that, at low levels of conversion of AMS, the purity of UD1 in the product was 92% as desired, but as the fractional conversion of AMS increased beyond 20%, the selectivity for UD1 decreased, thus rendering the L–L operation unsuitable for production of UD1 of 92+% purity at a high conversion level of AMS. They also developed a commercial method for producing 92+% UD1 by a solid acid catalyzed process. Later, Chaudhuri[2] described a liquid–liquid process for producing AMS dimers containing 93% UD1. The author, however, did not report the detailed kinetics of the L–L process. Perhaps that is the only information on the dimerization of AMS not available in the open literature and, to the best of our knowledge, no researcher to date has reported the kinetics of the L–L dimerization of AMS. The kinetic data will be useful for the design of reactors.

The present work was guided by the objective of determining the kinetics of the L–L dimerization of AMS. Along with the kinetics, attention was focused on the product distribution

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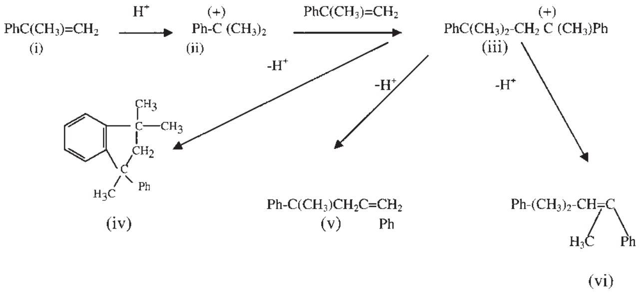
Correspondence concerning this article should be addressed to B. Chaudhuri at basabc@vsnl.net.



Scheme 1.

as well. In the present work, one liquid phase was an aqueous sulfuric acid solution of different strengths and the other liquid phase was 99.5% AMS containing some cumene impurity. The effects of the speed of agitation; catalyst concentration; temperature; and the presence of an additive (such as methanol, isopropanol, ethylene glycol, etc.), in the aqueous phase, in small concentration, and so forth, on the rate of dimerization and also on the selectivity of the desired dimer UD1 have been studied. The end users of AMS dimer now prefer UD1 purity of 93% (minimum) in the product. The aim of the present investigation was to look for an aqueous medium with sulfuric acid as the acidic material that would give a product dimer having UD1 at a concentration $>$ 93% at high levels of conversion of AMS. It was also thought that the L–L operation would allow the aqueous phase to be repeatedly reused in the process. The use of such an aqueous medium for dimerization of AMS will obviate the need to restrict the conversion level of AMS to within 10–12% in a process using only aqueous sulfuric acid as a catalyst. There will also be a substantial saving on separation because it will no longer be necessary to distill out a large quantity of unreacted AMS from the organic phase and recycle it back into the process. The results of the investigation are reported herein.

Some relevant information on the dimerization of AMS published in the patent literature is pertinent. Hersberger et al.[3] made first claims on the preparation of unsaturated dimers of AMS, substantially free of cyclic dimer by reacting AMS and aqueous sulfuric acids, and indicated concentration and temperature ranges of aqueous acids useful for obtaining unsaturated dimers. Later, Thurber[4] used phosphorous oxychloride or oxybromide and a small amount of strong mineral acids for making unsaturated dimers. This process could ease the commercial production of unsaturated dimers resulting from the reduced acid volume and, consequently, reduced reactor volume, so claimed the author. The process for making unsaturated dimers slowly evolved, in which liquid acidic media made way for solid acids as catalysts. In 2000 Andreevich et al.[5] claimed in a Russian patent that they could produce unsaturated dimers of AMS by reacting AMS with 70–75% sulfuric acid containing iron sulfate at temperatures in the range of 30–40°C. The process was claimed to have been carried out at a volume ratio of acid to the organic reactant of 0.32–0.38 to 100, and at the rate of no higher than 12%/h, to obtain a dimer that is used for control of polymeric chain increment.

There are a number of catalysts that have been tried in the dimerization of AMS at various reaction temperatures, even up to 443 K. An AMS conversion of 41 and 93% selectivity for UD1 was reported by Takahatake and Hasui[6] when they used montmorillonite catalyst at 418 K. Wygant[7] reported preparation of unsaturated dimers by treating AMS with clays. The yield was maximized with the help of reaction-directing compounds such as C_{1-10} alcohols, aldehydes, or ketones. Bateman[8] used H_2SO_4 as a catalyst for dimerization at 333 K with 40% yield. Heating AMS with 0.5–30 wt % formic acid produced dimers, according to Kosovtrev et al.[9]

Kawakami et al.[10] reported the dimerization of AMS using a catalytic amount of binary solid acids, such as Al_2O_3–TiO_2, TiO_2–ZrO_2, SiO_2–Al_2O_3, or acid clay at 30°C where, among the oligomeric products, UD1 and UD2 are the main components. Stegmann et al.[11] claimed in a patent that the dimerization of α-methylstyrene in 1,1,3-trimethyl-3-phenylindan as solvent, in the presence of Fulcat® at 383 K, gave 1,1,3-trimethyl-3-phenylindan as a product in 94.7% yield. Acidic terra alba or active terra alba also act as catalysts in 1,4-dioxane or aliphatic ethers according to Nippon Oils and Fats Co. Ltd. of Japan.[12] The presence of synthetic mica substituted by divalent metals may also induce dimerization of AAS (α-alkylstyrene), as claimed by Mitsui Petrochemical Industries Ltd.[13] Nippon Petrochemical Co. Ltd.[14] claimed that the use of 2-butoxyethanol (Butyl Cellosolve®) as a solvent gave improved selectivity over that of *n*-butanol for UD1, the unsaturated dimer of AMS. Unsaturated dimers of AAS can also be prepared by reacting it over cation-exchange resin of pore diameter 10^2–10^3 Å (Nittetsu Chemical Industries Co. Ltd.).[15]

In 1989 Chaudhuri and Sharma[1] reported a detailed study on various aspects of dimerization of AMS, such as kinetics and selectivities for the different products in the presence of cation-exchange resins, such as Amberlyst-15, K-2661, and Lewasorb AC 10 FT. Sun et al.[16] reported the dimerization of AMS on Amberlyst-15 and also on Nafion® perfluorosulfonic acid resin in three different microstructures. To compare the efficiency of different catalysts in nonpolar media such as cumene and polar media such as *p*-cresol, temperature-programmed desorption and thermogravimetric analysis were used. Harmer et al.[17] used Nafion® resin, a perfluorinated ion-exchange polymer, as a heterogeneous strong acid catalyst for a range of reactions; however, in nonpolar solvents or for gas-phase reactions the activity is limited because of the extremely low surface area of the polymer beads ($<$0.02 $m^2\ g^{-1}$). This new material has been developed using an in situ sol–gel technique wherein solutions of Nafion® resins are mixed with soluble silicon sources to form a gel, which is dried to a clear, hard, glasslike material. These new porous nanocomposites offer the potential for significantly enhanced activity resulting from the increased accessibility of the Nafion® resin–based acid sites. It appears from the foregoing discussion that no systematic investigation has been done on the detailed kinetics of the dimerization of AMS in heterogeneous L–L mode using a commonly used catalyst such as H_2SO_4. The objective of the present work was to determine the reaction regime for the dimerization reaction, the rate constants at different temperatures and catalyst concentrations, and also the product distribution.

Experimental

Experiments were conducted in a 0.10-m internal diameter (ID) fully baffled mechanically agitated contactor, a schematic diagram of which is given in Figure 1. A six-bladed glass-disk turbine impeller was used for agitation. All the experiments

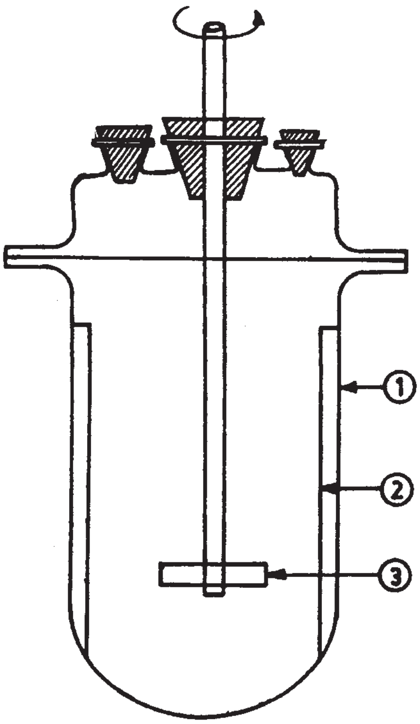


Figure 1. Sectional view of the mechanically agitated reactor: (1) glass vessel; (2) baffles; (3) turbine agitator.

were carried out at the desired temperature by placing the reactor in a constant temperature bath.

At first, a known volume of the aqueous phase was placed in the reactor and slowly heated to the reaction temperature. For reactions in which methanol was used, the mixture of aqueous acid phase and methanol was placed in the reactor. The organic phase, which was basically AMS, was heated to the same temperature in a separate vessel. Subsequently, the organic phase was carefully transferred with the help of a long funnel into the reactor, and the agitation of the L–L system was started. This was taken as the starting time of the reaction.

The L–L system readily separated into two distinct phases as soon as the agitation was stopped. Samples (2 mL) from the organic phase were collected at definite time intervals and analyzed by gas chromatography. Typical conditions used for analysis were as follows: injector and detector temperatures: 523 K each; oven temperature: 373 K (zero isothermal time), raised to 523 K with a ramp rate of 4 K/min; carrier gas, N_2 gas; and rate of flow of N_2, approximately 20 mL/min.

AMS of purity $> 99\%$, procured from Lancaster Synthesis Ltd. (Morecambe, UK), was used in some crucial experiments. A commercial variety of 97% AMS with cumene and *tert*-butylbenzene as impurities, manufactured by Herdillia Chemicals Ltd. (now Schenactady Herdillia), Navi Mumbai, India, was procured through a local agent. In most experiments reported here, this commercial-grade AMS was used. It was confirmed that the rates of dimerization and product selectivities were practically the same for both grades of AMS. Sulfuric acid, methanol, isopropanol, ethylene glycol, and other reagents, of AR grade, were procured from S.D. Fine Chemicals (Mumbai, India). Aqueous acidic solutions were made using distilled water; it was confirmed, however, that the dimerization reactions conducted with aqueous acidic solutions prepared from tap water gave almost the same rates and product selectivities as those conducted with aqueous acidic solutions prepared from distilled water. Mass balance was checked in all experiments and excellent reproducibility in duplicate sets was obtained.

Table 1. Dimerization of α-Methylstyrene (AMS, 160 g) with 1 g (98%) H_2SO_4*

Components in the Reaction Mixture	Mass Percentage
AMS	4
UD1	10
UD2	21
Saturated dimer	65

*Reaction time: 30 min; average reaction temperature: 393 K.

Results and Discussion

Initial experiments on dimerization with dissolved H_2SO_4 in AMS were conducted at a temperature of 333 K. In 3 h, practically no dimer formation was observed. It could be concluded, therefore, that dissolved H_2SO_4 present in AMS did not catalyze the dimerization at all. In subsequent experiments, 160 g of AMS was stirred with 1 g of 98% H_2SO_4. As soon as the stirring of the AMS with H_2SO_4 was started, the whole aqueous organic dispersion became reddish in color. Within 5 min, the liquid temperature increased from 303 to 408 K. Samples were withdrawn after 30 min and analyzed, results of which analysis are given in Table 1.

It is clear that the dimerization with 98% H_2SO_4 becomes difficult to control and the reaction goes to the so-called runaway condition. Moreover, the product distribution indicates that the saturated indanic dimer is formed in a much larger concentration when the H_2SO_4 concentration is high. Previous results[2] suggest that the presence of water in H_2SO_4 in larger proportions helps to reduce the speed of reaction, thereby facilitating the task of controlling the reaction temperature. Also, the presence of water suppresses the formation of the saturated indanic dimer and improves the ratio of UD1:UD2. Subsequent experiments were therefore conducted with aqueous H_2SO_4 solutions with strengths varying from 7.5 to 13.33 N.

Effects of speed of agitation on the rate of dimerization

It was stated earlier that the dual objective of the present work was

- to study the kinetics of dimerization with aqueous H_2SO_4 in a two-phase mode of operation, and
- to establish reaction conditions for obtaining maximum UD1:UD2 ratio with the smallest possible quantities of saturated indanic dimer

The first step toward studying the kinetics of the L–L reaction is to ascertain the effect of speed of agitation on the rate of dimerization. If diffusional limitations are present, the variation in the speed of agitation will clearly affect the rate. On the other hand, for reactions that are controlled by intrinsic kinetics, the effect of speed of agitation on the rate will be practically negligible.

Under otherwise uniform conditions the dimerization reac-

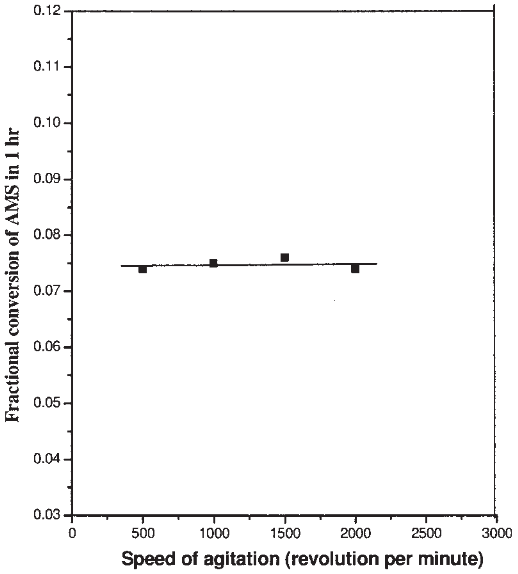


Figure 2. Fractional conversion of AMS in 1 h 353 K at different speeds of agitation.

tion was conducted at 353 K at speeds of agitation varying from 500 to 2000 rpm and the fractional conversion of AMS as achieved within 1 h were experimentally measured. The results are presented in Figure 2. One clearly finds that the speed of agitation had practically no effect on the rate of dimerization at 353 K, thereby suggesting that intrinsic kinetics might be important. The temperature of 353 K, instead of lower operating temperatures such as 333 or 343 K, was selected to study the effect of speed of agitation because, at higher temperatures, intrinsic rates would be higher, thus inviting, if any, mass-transfer limitations in the process.

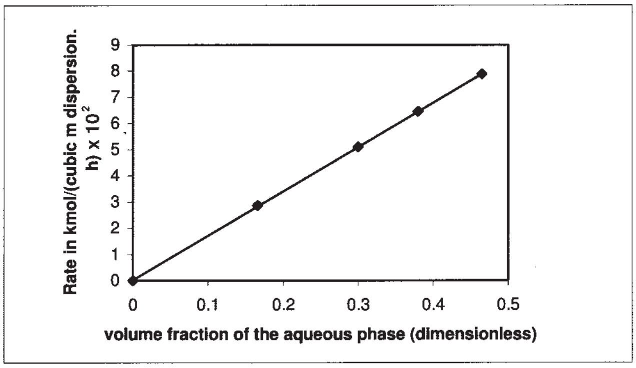
Effect of the variation in aqueous-phase volume

In the L–L dimerization of AMS, the locale of the reaction is the aqueous phase and for a kinetically controlled process an increase in the aqueous-phase volume will proportionally increase the rate of reaction expressed in kmol/s. For example, if the aqueous phase (locale of the reaction) volume is doubled, for the same volume of the organic phase under otherwise uniform conditions, the rate of dimerization in kmol/s will be enhanced by a factor of 2. This could be verified by conducting the dimerization reaction. The rates of dimerization in kmol/(m^3 dispersion h) as a function of volume fraction of the aqueous phase could be correlated by Figure 3 and excellent correlations were obtained, suggesting that the reaction is indeed kinetically controlled.

Determination of the order and the rate constants

There are two general methods for determining the kinetics of reactions that are intrinsically kinetically controlled: (1) differential method and (2) integral method. In the present work, the integral method of analysis has been adopted.[18,19]

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted concentration vs. time curve with the experimental concentration vs. time data. If the fit is unsatisfactory, another rate equation is suggested and tested.



Correlation coefficient : 0.99945
Standard deviation: 0.12072

Figure 3. Rate of dimerization (kmol/m^3 dispersion.h) as a function of volume fraction of the aqueous phase (test for kinetically controlled regime).

Order and the rate constants for the L–L dimerization of AMS

Heterogeneous solid acid–catalyzed dimerization of AMS is known to be first-order. As a first guess we assumed that the reaction was first-order for which the following relationship holds:

$$-\ln(1 - X_A) = k_{1st}t \tag{1}$$

where X_A is the fractional conversion of the reactant AMS, k_{1st} is the first-order rate constant, and t is time. Linear plots of $-\ln(1 - X_A)$ vs. t passing through the origin (Figure 4) show that the dimerization is indeed first-order. The rate constants at different temperatures (333, 343, and 353 K) are given in Table 2. A linear plot of ln k_{1st} vs. $1/T$ (Figure 5) gives the value of activation energy that is about 52.3 kJ/mol. In view of the fact

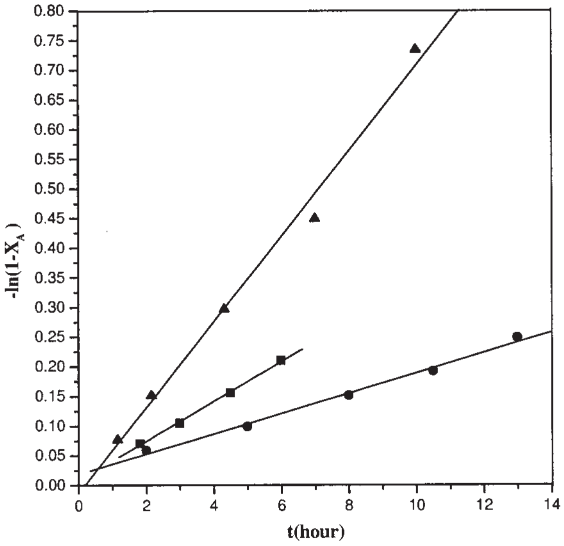


Figure 4. Test of first-order kinetics for liquid–liquid dimerization of AMS.

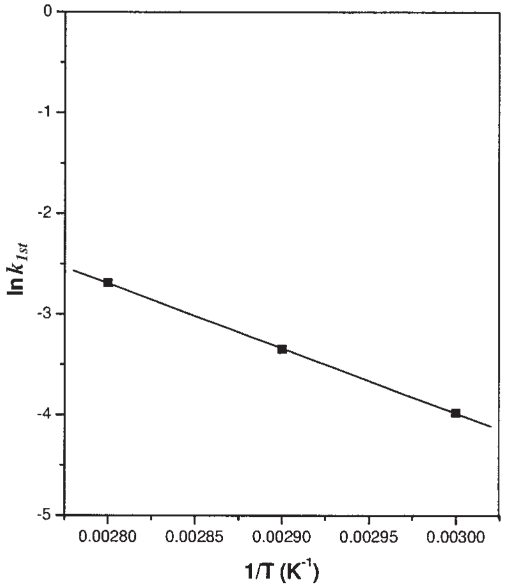
Table 2. Rate Constant for Dimerization of AMS at Different Temperatures

T (K)	k (h^{-1})	ln k
333	0.0187	−3.98
343	0.035	−3.35
353	0.068	−2.69

that the solubility of AMS in aqueous acid solutions is likely to be influenced by a change in temperature and no attempt to correlate the AMS solubility in the aqueous phase with temperature has been made in the present study, the activation energy reported here is "apparent" or "global" activation energy, and not the "true" activation energy, characteristic of a process controlled by an intrinsic chemical reaction.

Explanation for the first-order dependency from a plausible mechanism

AMS must cross over the L–L interface and then interact with the hydrogen ion, leading to the formation of carbocation. In aqueous solution, hydrogen ion remains as hydronium ion, H_3O^+. To provide a consistent mechanism, it is assumed that the hydrophobic AMS is not attacked by H_3O^+ because of the water molecule associated with H^+ and also because of the steric factor. H^+ released from the hydronium ion interacts with AMS and forms the carbocation. One AMS can interact with one H^+ only; however, there may be two, three, or more H^+ available for the interaction. The suggested mechanism is required (1) to show first-order dependency of AMS on the rate of formation of the dimer, (2) to explain very low rates to be realized when the acid is dilute, and (3) to provide a reasonable explanation for the variation of experimentally determined rate constants with change in acid strength. Keeping the foregoing points in mind, the following mechanistic scheme is devised:



Correlation coefficient: -0.99991
Standard deviation: 0.01225

Figure 5. Arrhenius plot for the dimerization of AMS.

Table 3. Effect of Acid Concentration on the Rate Constant Values for Dimerization of AMS*

Concentration of Acid (N)	Rate Constant (h^{-1})
7.5	8.8×10^{-3}
10	6.9×10^{-2}
13.33	5.0×10^{-1}

*Temperature: 353 K.

$$[AMS] + [H^+] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [AMS^+] \tag{2}$$

$$[AMS] + 2[H^+] + H_2O\ (\text{excess}) \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [AMS^+] + H_3O^+ \tag{3}$$

$$[AMS] + 3[H^+] + H_2O\ (\text{excess}) \underset{k_6}{\overset{k_5}{\rightleftharpoons}} [AMS^+] + 2H_3O^+ \tag{4}$$

and so on. Additional equations like Eqs. 2–4 can be written, where the number of hydrogen ions will be 4, 5, 6, and so forth.

Formation of $[AMS2^+]$ occurs by the following reaction:

$$[AMS^+] + [AMS] \underset{k'}{\overset{k}{\rightleftharpoons}} [AMS2^+] \tag{5}$$

Once $[AMS2^+]$ forms, it has only one course left: to yield the dimers, generally designated AMS2 in the mechanism. AMS2 means UD1, UD2, and SD combined.

$$[AMS2^+] \xrightarrow{k''} AMS2 + H_3O^+ \tag{6}$$

The following equilibrium is also to be considered:

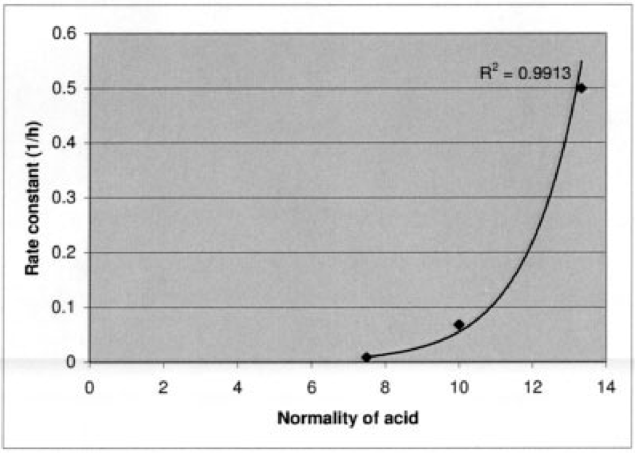


Figure 6. Rate constant as a function of acid concentration.

Table 4. AMS Dimerization with Aqueous H_2SO_4 Acid*

H_2SO_4 Concentration in Aqueous Phase (% w/v)	Time (h)	AMS Conversion (%)	Product Distribution (mass %)				
			UD1	UD2	SD	PDMC	UD1:UD2
49	2.16	4	2.08	0.28	Nil	1.6	89:11
	4.83	8.3	5.8	0.86	0.05	1.6	87:13
	8	14	10.5	1.4	0.099	1.54	88:12
	10.5	17.5	13.5	1.8	0.13	1.52	88:12
	13	22	18	2.42	0.17	1.54	88:12
	30	42	35.6	4.4	0.25	1.65	89:11

*H_2SO_4 (98%) = 150 g; aqueous phase = 300 cm^3; acid concentration = 0.49 g/cm^3 = 5 mol/L = 10 N; AMS = 300 g = 345 cm^3; aqueous to organic phase ratio = 300:345 = 1:1.15; volume fraction of aqueous phase = 0.465; volume fraction of organic phase = 0.535; temperature = 333 K.

$$H^+ + H_2O \rightleftharpoons H_3O^+ \tag{7}$$

where

$$K_{eq} = [H_3O^+]/[H^+][H_2O] \tag{8}$$

Now, the rate of formation of $[AMS^+]$ can be obtained by combining Eqs. 2–4 (and many more of that type with varying numbers of H^+) and Eq. 5. We will then have the following:

$$d/dt[AMS^+] = k_1[AMS][H^+] + k_3[AMS][H^+]^2 + k_5[AMS] \times [H^+]^3 + \cdots - k_2[AMS^+] - k_4[AMS^+][H_3O^+] - k_6[AMS^+][H_3O^+]^2 - \cdots - k[AMS^+][AMS] + k'[AMS2^+] \tag{9}$$

The rate of formation of $[AMS2^+]$ is

$$\text{Rate} = d/dt[AMS2^+] = k[AMS^+][AMS] - k'[AMS2^+] - k''[AMS2^+] \tag{10}$$

At steady state, the time derivatives of $[AMS^+]$ and $[AMS2^+]$ will vanish.

Applying this principle, we get from Eq. 10

$$[AMS2^+] = \frac{k[AMS^+][AMS]}{k' + k''} \tag{11}$$

The rate of formation [AMS2], given by Eq. 6, is

$$\text{Rate} = k''[AMS2^+] \tag{12}$$

By combining Eqs. 9 and 11, denoting the overall constant associated with the product, $[AMS^+][AMS]$, by a single constant k_t, and setting the time derivative with respect to $[AMS^+]$ equal to zero, we obtain

$$[AMS^+] = \frac{[AMS]\{k_1[H^+] + k_3[H^+]^2 + k_5[H^+]^3 + \cdots\}}{(k_2 + k_4[H_3O^+] + k_6[H_3O^+]^2 + \cdots) + k_t[AMS]} \tag{13}$$

By substituting $[AMS2^+]$ from Eq. 11 into Eq. 12 using $[AMS^+]$ from Eq. 13, and grouping all the constants together and calling it K, we have

Rate of formation of dimer

$$= \frac{K[AMS]^2\{k_1[H^+] + k_3[H^+]^2 + k_5[H^+]^3 + \cdots\}}{(k_2 + k_4[H_3O^+] + k_6[H_3O^+]^2 + \cdots) + k_t[AMS]} \tag{14}$$

It is expected that the constants $k_1, k_3, k_5 \cdots$ will have similar values and, therefore, that part of the numerator involving H^+ in Eq. 14 will have a functional form that is a product of $[H^+]$ and an exponential term involving $[H^+]$. At low $[H^+]$, this part will have low values, although at higher $[H^+]$ the values will be very high. This has a direct influence on the rates of dimerization. At lower acid concentrations, the reaction does not proceed; at higher acid concentrations, however, extremely high rates of dimerization are achieved.

The chemistry of dimerization is such that once $[AMS^+]$ forms, it does not revert to AMS. This means the constants k_2, k_4, $k_6 \cdots$ will be insignificant compared to k_t, particularly at high acid concentrations. In this situation, Eq. 14 predicts first-order dependency of the rate of dimerization on the AMS concentration, as verified in our experiments.

At lower acid concentrations, the constants k_2, k_4, $k_6 \cdots$ involving $[H_3O^+]$ are likely to become more significant. Moreover, $[H_3O^+]$, a product of $[H_2O]$ and $[H^+]$, given by Eq. 8,

Table 5. AMS Dimerization with Aqueous H_2SO_4 Acid*

H_2SO_4 Concentration in Aqueous Phase (% w/v)	Time (h)	AMS Conversion (%)	Product Distribution (mass %)				
			UD1	UD2	SD	PDMC	UD1: UD2
49	1.83	6.9	4.51	0.68	0.05	1.67	86.9:13.1
	3	10	7	1	0.08	1.58	87.5:12.5
	4.5	14.5	10.7	1.77	0.13	1.65	85.8:14.2
	6	19	14	2.5	0.25	1.65	85:15
	15	41	34.1	5.4	0.30	1.69	86.3:13.7

*H_2SO_4 (98%) = 150 g; aqueous phase = 300 cm^3; acid concentration = 0.49 g/cm^3 = 5 mol/L = 10 N; AMS = 300 g = 345 cm^3; aqueous to organic phase ratio = 300:345 = 1:1.15; volume fraction of aqueous phase = 0.465; volume fraction of organic phase = 0.535; temperature = 343 K.

Table 6. AMS Dimerization with Aqueous H_2SO_4 Acid*

H_2SO_4 Concentration in Aqueous Phase (% w/v)	Time (h)	AMS Conversion (%)	Product Distribution (mass %)				
			UD1	UD2	SD	PDMC	UD1:UD2
49	1.16	7.4	4.3	0.63	0.35	1.8	87:13
	2.16	14	9.9	1.6	0.25	1.8	86:14
	4.32	25.7	21.3	3.65	0.35	1.7	85:14.6
	10	52	40.67	7.43	0.61	2.0	85:15.5

*H_2SO_4 (98%) = 150 g; aqueous phase = 300 cm^3; acid concentration = 0.49 g/cm^3 = 5 mol/L = 10 N; AMS = 300 g = 345 cm^3; aqueous to organic phase ratio = 300:345 = 1:1.15; volume fraction of aqueous phase = 0.465; volume fraction of organic phase = 0.535; temperature = 353 K.

becomes large because of larger quantities of water necessary to achieve lower acid concentrations. A large value of the denominator causes the rate of dimerization of AMS to reduce drastically, which has been verified experimentally.

Effect of acid concentration

For the L–L dimerization, the concentration of H_2SO_4 will affect the rate constant of the reaction. To determine the variation of rate constant with acid concentration at a temperature of 353 K, experiments were conducted as described earlier. Results are given in Table 3 and also in Figure 6. From Figure 6 we find that the rate constant increases exponentially with the acid concentration. An explanation for the enhancement of the rates of dimerization and thus of the rate constants with an increase in acid concentrations has been given in the preceding section, based on the mechanism developed for the L–L dimerization process.

Product distribution

As described earlier in the introduction, the two-phase dimerization of α-methylstyrene gives mainly the following products:

(1) The unsaturated dimer 2,4-diphenyl-4-methyl-1-pentene (UD1)

(2) The unsaturated dimer 2,4-diphenyl-4-methyl-2-pentene (UD2)

(3) 1,1,3-trimethyl-3-phenylindan, called the saturated dimer (SD)

Other than those listed above, two more compounds are formed in the process. One is phenyl dimethyl carbinol (PDMC), formed by the reaction of AMS carbocation with water. This alcohol is important as a perfumery chemical. In the present study, however, no attempt was made to optimize the conditions necessary for the production of PDMC. The focus was to ascertain optimum conditions for the production of UD1. The other substance formed in the process is cumyl methyl ether (CME), formed on reaction of AMS carbocation with methanol (when methanol was added as an additive to improve the selectivity for UD1). The concentration of CME formed on reaction was determined in the present study; no attempt was made to optimize conditions for selectively producing the material. It is pertinent to mention, however, that the compound CME is like methyl *tert*-butyl ether (MTBE) and may have octane-boosting characteristics, when used as an additive in gasoline.

Product distributions are given in Tables 4, 5, and 6 at different levels of conversion. It is clear from the tables that the ratio of UD1:UD2 remains substantially constant at different levels of conversion of AMS at temperatures ranging between 333 and 353 K. The dimerization at temperatures $>$ 353 K was not investigated because it was felt that the ratio of UD1 to UD2 would be adversely affected at higher reaction temperatures. The product distribution also suggests that the isomerization of UD1 to UD2 was an extremely slow process and the major reaction was the formation of the dimer. It should be pointed out that for the dimer to act as an effective chain terminator, the UD1 concentration must be $\geq$93%. The two-phase dimerization without any additive, however, did not produce a dimer of the desired quality. Chaudhuri and Sharma[1] and Chaudhuri,[2] investigated the addition of methanol into the aqueous phase, which showed the efficacy of alcohol in improving the UD1:UD2 ratio (results are given in Table 7). In the present study, we have done similar experiments by adding 1,2-propylene glycol and ethylene glycol in the aqueous phase so as to increase the UD1:UD2 ratio, and the results are given in Tables 8 and 9. It is found that the addition of glycols in the liquid–liquid dimerization improved the selectivity for UD1 and typical ratios of UD1:UD2 are similar to the required value of 93:7 for both additives.

Table 7. Product Distribution in the Dimerization of AMS in L–L Mode (Aqueous H_2SO_4 Catalyst and Methanol)*

Quantity of Methanol (mL) Added to 300 mL Aqueous Phase	Time (h)	AMS Conversion (%)	Product Distribution (mass %)					
			UD1	UD2	SD	CME	PDMC	UD1:UD2
75 (20% v/v)	1	9.8	4.0	0.3	0.04	4.1	1.5	93:7
	2.5	18.9	13.5	1.1	0.04	3.8	1.6	92.4:7.6
	7	45.0	37.4	3.0	0.05	3.3	1.2	92.6:7.4
100 (25% v/v)	1	19	3.35	0.21	0.03	12.9	2.6	94:6
	2.66	28	13.67	0.92	0.03	11.3	2.6	93.6:6.4
	7	55	43.74	3.27	0.03	7.2	1.7	93:7
	10	67	57.0	4.6	0.03	6.9	1.4	92.5:7.5
125 (29.4% v/v)	1	22	4.4	0.3	0.05	14.7	2.5	93.6:6.4
	2.6	33	18.1	1.5	0.05	13.9	2.5	92.3:7.7
	7	64	47.8	3.8	0.05	13.8	2.5	92.6:7.4

Note: Table reproduced from Chaudhuri.[2]
*Aqueous phase: 49% (w/v) H_2SO_4, 300 mL; AMS: 345 mL; temperature: 353 K; speed of agitation: 2000 rpm.

Table 8. Liquid–Liquid Dimerization of AMS: Effect of 1,2-Propylene Glycol as an Additive on Product Distribution*

Component	Mass %	% UD1 in Product	UD1:UD2
Glycol	0.284	93.1	93.1:6.9
TBB	1.198		
AMS	39.886		
PDMC	0.969		
Unknown	0.25		
Unknown	0.349		
Unknown	0.391		
Saturated dimer	0.143		
UD1	52.755		
UD2	3.775		

*Aqueous phase: 37.5 g 98% H_2SO_4 dissolved in 75 cm^3 solution + 25 cm^3 1,2-propylene glycol [CH_3–CH(OH)–CH_2(OH)]. Organic phase: AMS, 87 cm^3 (~75 g); temperature = 353 K; rpm = 800. Sample after 6.5 h.

The question remains as to why alcohols as additives improve the ratio of UD1:UD2. A plausible explanation, not yet reported in the literature, might be: primary alcohols and glycols readily interact (possibly through hydrogen bonding) with the terminal methyl group in the carbocation [Scheme 1 (iii)], thus stabilizing it, and leading to the formation of UD1. The steric factor caused by the presence of the phenyl group along with the methyl group attached to the same carbon atom facilitates the proton abstraction, thereby favoring the formation of UD1.

Conclusions

The liquid–liquid dimerization of AMS conforms to the kinetically controlled regime under the experimental conditions under investigation (temperature: 333–353 K; acid strength: 7.5–13.33 N; speed of agitation: 500–2000 rpm). The rate constants are reported. The product distribution was found to improve for UD1 with the addition of propylene glycol and ethylene glycol. The method can be adopted for commercial production of AMS dimer, especially high-purity UD1.

Notation

k_{1st} = first-order reaction rate constant used in Eq. 1
$k_1, k_3, k_5 \cdots$ = constants for the forward reactions used in Eqs. 2–4
$k_2, k_4, k_6 \cdots$ = constants for the backward reactions used in Eqs. 2–4
k = constant for the forward reaction used in Eq. 5
k' = constant for the backward reaction used in Eq. 5
k'' = constant for the irreversible reaction used in Eq. 6
K = overall constant used in Eq. 14
K_{eq} = equilibrium constant used in Eq. 8
k_t = constant involving k, k', and k'', used in Eq. 13
t = time, s
X_A = fractional conversion, unitless

Table 9. Liquid–Liquid Dimerization of AMS: Effect of Ethylene Glycol as an Additive on Product Distribution*

Component	Mass %	% UD1 in Product	UD1:UD2
Unknown	0.072	92.9	92.9:7.1
Unknown	0.147		
AMS	65.383		
PDMC	1.973		
Unknown	0.313		
Unknown	0.134		
Unknown	0.149		
Unknown	0.247		
SD	0.17		
UD1	28.064		
UD2	1.959		
Unknown	0.825		

*Aqueous phase: 37.5 g 98% H_2SO_4 dissolved in 75 cm^3 solution + 25 cm^3 ethylene glycol [CH_2(OH)–CH_2(OH)]. Organic phase: AMS, 87 cm^3 (~75 g); temperature = 353 K; rpm = 800. Sample after 6 h.

Acronyms

AMS = α-methylstyrene
AMS2 = α-methylstyrene dimers (general)
CME = cumyl methyl ether
PDMC = phenyl dimethyl carbinol
SD = saturated dimer, structure given in Scheme 1 in the text
UD1 = unsaturated dimer 1, structure given in Scheme 1 in the text
UD2 = unsaturated dimer 2, structure given in Scheme 1 in the text

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