Survey of Propane Pyrolysis Literature

Ara G. Volkan and Gary C. April*

Chemical and Metallurgical Engineering Department, The University of Alabama, Tuscaloosa, Alabama 35486

Hydrocarbon pyrolyses have occupied a central role in the development of gas kinetics, first, because of their great economic potential, and secondly, because their relative molecular simplicity has been thought to offer the prospect of reasonably straightforward elucidation of the processes involved. Hydrocarbon pyrolyses to produce olefins, diolefins, and aromatics are the main processes of today's petrochemical industry. The purpose of this survey is to review a sub-set of this broad field of study—the thermal decomposition of propane. More than a decade ago it would have been relatively easy to review the entire hydrocarbon pyrolysis field, but the number of studies published in the past ten years restricts this review to the field of propane pyrolysis. A summary of recently reported data and results does not exist. Therefore, the intent of this review is to compile the propane pyrolysis data and to present the available knowledge to those interested in hydrocarbon pyrolysis studies and the positive impact that may occur within the petrochemical industry.

Introduction

For a long period of time the issues involving pyrolysis experiments were somewhat confused. As a result of inhibition experiments, notably those involving additions of NO and C_3H_6, it was thought that decomposition was achieved by both molecular and radical chain routes. Researchers finally established the fact that there were no significant molecular reactions in the pyrolysis of hydrocarbons. The main body of evidence accumulated during the period 1957–1965 has already been reviewed (80). Its validity received striking confirmation in the observations of Martin, Niclause and their co-workers (59, 63, 69) in that pyrolyses of propane, isobutane, and isopentane are effectively and totally suppressed in PbO-coated vessels of a high surface to volume ratio if a trace of oxygen is present. Since molecular processes could hardly be inhibited under these conditions, it follows that the reactions are entirely free radical in nature.

All in the field of pyrolysis agree that the reactions can basically be described in terms of the Rice–Herzfeld radical chain mechanisms (83) and that, in general, the chains are long. However, the increasing application of gas chromatography has revealed that the appropriate Rice–Herzfeld scheme must always be extended and modified to account for the products observed. Also, it is established that the effect of surfaces and other impurities must be taken into consideration. Finally, temperatures and pressures prevailing during the experiment may further complicate the situation by giving rise to polymerization and inhibition reactions. Fortunately, these problems are now better understood and over the past ten years a body of work has appeared which can satisfactorily interpret these problems.

Most of the studies have been carried out at low (25–400 °C) and medium (400–800 °C) temperature ranges. These studies employed conventional (static system) and a variety of nonconventional reactors and techniques. Among the latter, studies at the plant level are most important. The high-temperature (greater than 800 °C) studies almost always employed the shock-tube technique and tend to be much more scattered and therefore less reliable despite the practical importance of such reactions. Because of their practical importance and current interest in the area, studies at the plant level and on the shock-tube pyrolysis of propane will be presented first followed by a review of static investigations and other techniques. Studies about the effects of the diluents, walls, and impurities on the pyrolysis of propane will also be reviewed.

A Study At Plant Level

There exists a body of literature on propane cracking at the plant level. Kinetic data and mechanisms are not subjects of these discussions with the possible exception of Davies and Farrell (21), who derived first-order, general kinetic equations for the cracking of hydrocarbons from industrial data, and Van Damme et al. (98).

Van Damme et al., studied the product distribution and kinetics of the thermal cracking of propane and propane-propylene mixtures for a temperature range of 700–850 °C, exit total pressures from 1.2 to 2 atm absolute, and steam dilutions of 0.4 and 1.0. The study was conducted in a pilot plant at or very near the operating conditions of the petrochemical industry, and it is unique in its field.

The product distribution profiles derived from the pilot plant were in excellent agreement with the industrial plant results. Propylene was found to decrease the decomposition rate of propane as well as decreasing the yield of ethylene and butadiene while increasing the yields of C_5+ products. Calculations used in deriving the overall order and the activation energy as well as the simulation of the proposed mechanism employed pseudo-isothermal and nonisothermal analyses. Both approaches resulted in first-order kinetics and predicted for the overall disappearance of propane, $K = 1.06 \times 10^{11} \exp(-51\,000/RT)$ s^{-1} which are in excellent agreement with the existing literature ($A = 10^{11}$ to 10^{14} s^{-1}, $E = 50\,000$–$70\,000$ cal/mol; see Tables I and II). (Tables I–III appear as supplementary material only. See the paragraph at the end of the paper regarding this material.)

The proposed reaction scheme was also unique. Instead of listing the intermediate radical chain reactions which led to the observed products, they proposed an overall molecular scheme for gas cracking which was used to compute a material balance on the observed products. The proposed steps and kinetic data used are listed in Table IV.

Shock-Tube Pyrolysis of Propane

Benson (3) presented shock-tube results on the pyrolysis of propane for a temperature range of 830–1180 °C. Both uncatalyzed and catalyzed (H_2S) homogeneous decompositions were studied. Overall reactions leading to the decomposition of propane occurred via two routes with roughly equal importance
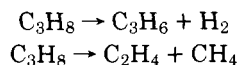
$$C_3H_8 \rightarrow C_3H_6 + H_2$$
$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

Table IV. Activation Energy and Frequency Factor Data for Several Reactions Occurring in Propane Pyrolysis Mechanisms

Reactions	A (s^{-1}) or a (kmol^{-1} M^3 s^{-1})	E (cal/mol)
$C_3H_8 \rightarrow C_2H_4 + CH_4$	1.6×10^9	44 000
$C_3H_8 \rightarrow C_3H_6 + H_2$	1.4×10^9	44 000
$2C_3H_8 \rightarrow C_2H_6 + C_4H_{10}$	2.2×10^9	54 000
$2C_3H_8 \rightarrow C_3H_6 + C_2H_6 +$ CH$_4$	1.1×10^9	48 000
$C_3H_8 + C_2H_4 \rightarrow C_3H_6 +$ C_2H_6	3.0×10^{10} a	40 000
$C_2H_6 \rightarrow H_2 + C_2H_4$	8.0×10^{13}	60 000
$2C_2H_6 \rightarrow C_2H_4 + 2CH_4$	4.0×10^{12}	67 000
$2C_3H_6 \rightarrow 3C_2H_4$	1.3×10^{10}	50 000
$C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4$	1.0×10^{15}	60 000
$C_3H_6 \rightarrow C_2H_2 + CH_4$	1.4×10^{10}	50 000
$C_2H_4 + H_2 \rightarrow C_2H_6$	1.0×10^{14}	52 000
$C_2H_4 \rightarrow C_2H_2 + H_2$	6.0×10^{13}	76 000
$3C_2H_4 \rightarrow 2C_3H_6$	1.3×10^{11}	45 000
$2C_2H_2 \rightarrow C_4$ Product	6.0×10^{13} a	45 000
$C_2H_2 + 2H_2O \rightarrow 2CO + 3H_2$	3.5×10^{11}	62 000
$C_2H_2 + C_3H_6 \rightarrow C_5$ product	9.0×10^{16} a	64 000

Propylene subsequently converted, almost stoichiometrically, to ethylene and acetylene. The free-radical scheme describing the first-order mechanism is presented in Table I. The product distribution does not agree with that of other studies which will be presented later with the exception of Van Damme et al. (98). Almost all of these works report a high yield of propylene whereas Benson reports acetylene and ethylene formations from propylene even during runs with reactions of 0.1 ms.

Lifshitz and Frenklach (54) gave a decomposition mechanism for propane over a temperature range of 800–1000 °C at 200 Torr. The scheme does not include the steps for the decomposition of ethylene and propylene to yield allene, propyne, and acetylene. These steps become important over 1000 °C and the proposed mechanism does not represent the system above this temperature. The complete mechanism is given in Table II. It is shown that this scheme together with the rate expressions given represents the system extremely well at low extents of reaction. Most of the data were taken from their 29-step mechanism (76) which was suitable for lower temperatures and was essentially the same as the present one except that 18 recombination reactions were eliminated since they were not important at high temperatures.

Static Systems

(a) Historical. Before 1960 there were a number of studies concerning the pyrolysis of propane. All of these studies used a quartz vessel whose temperature was controlled by a large stainless steel block, that is, the conventional static system. The pioneers in this field were Pease (76), Marek and McCluer (58), Paul and Marek (75), Pease and Durgan (77), Rice (82), Frey and Hepp (27), Dintess and Frost (22–24), Steacie and Puddington (89), Hobbs and Hinshelwood (34), and Ingold et al. (35). All of these studies were conducted in the low (25–400 °C) temperature ranges. Collectively they come to the conclusion that the overall decomposition is a homogeneous and first-order reaction progressing with free radicals. Although considerable debate was going on about the existence of molecular reactions, the proposed mechanisms entirely consisted of free radical reaction steps. The one proposed by Rice (82) is of historical interest to us and is given in Table I. By 1961 the fact that pyrolysis reactions proceed by radical chain mechanisms was firmly established in the works of Eltenton (25), Kuppermann and Larson (48), and Purnell and Quinn (79).

(b) Post-1960 Studies. Laidler et al. (49) studied propane pyrolysis for a temperature range of 530–670 °C at pressures up to 600 mm. Their main purpose was to examine the exact nature of initiation and termination reactions. They concluded that the decomposition was first order and homogeneous and proceeded by a free-radical mechanism. A new development was the proposal that at low pressures and high temperatures (above 650 °C) the overall rate of decomposition became $^3/_2$ order. Both mechanisms are given in Table II. Also, for packed vessels the order of the decomposition appeared to be 1.25.

Martin et al. (60) studied propane pyrolysis to determine the effect of the S/V (surface to volume) ratio on the reaction. This experiment was conducted to verify or to refute the claims of Voevodsky (99). In a propane pyrolysis study, Voevodsky observed that changes in the S/V ratio changed the rate of propane pyrolysis. No such effect was found. The overall activation energy was also measured to be 67 000 cal/mol for a 545–650 °C temperature range. The important conclusions of this study are given in Table I.

Leathard and Purnell (53) investigated propane pyrolysis for a temperature range of 510–560 °C. They characterized the stoichiometry of the reaction as

$$(1 + a)C_3H_8 = H_2 + C_3H_6 + a(CH_4 + C_2H_4)$$
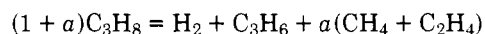
where a was found to be slightly temperature dependent but independent of pressure. A free-radical mechanism was proposed which gave an excellent account of the observed products. In this study, however, a quantitative simulation of the mechanism fails to reproduce product distribution. This result led to further investigations which indicated that even at very low conversions (0.1%) self-inhibition (recombination of decomposition products and radicals to form the original compounds) in propane pyrolysis played an important role. The mechanism was revised and is given in Table I. In summary, this study concluded that the S/V does not change the rate of the reactions, the observations of Martin et al. (61) about self-inhibition are correct, and the orders of 1.2–1.3 found in the two studies discussed above are correct.

Leathard and Purnell (52) followed their propane pyrolysis study with a study for a 441–500 °C temperature range. They studied primarily the isomerization step; (kinetic data given in Table I).

$$i\text{-}C_3H_7\cdot + C_3H_8 \rightarrow n\text{-}C_3H_7\cdot + C_3H_8$$
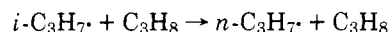
They also discovered that increases in the S/V ratio at this temperature range decreased the decomposition rate and increased the apparent order. Finally, below 450 °C the self-inhibition effect was removed. The mechanism proposed for the higher temperature range was an excellent approximation if the isomerization and wall reactions were included in the scheme given in Table I.

The Reactions of Photo-Sensitized Propane

(a) Historical. Before 1960 the mercury photosensitized decomposition of propane was studied by Steacie and Dewar (88), Darwent and Steacie (20), and Bywater and Steacie (14). This technique is no different from the conventional static system except that the reaction is initiated by excited mercury atoms and/or by a beam of light with a known energy. Studies in this field are included since their results can be compared and contrasted to the results of conventional experiments. The mechanism for propane decomposition proposed by Bywater and Steacie (14) is included in Table I. A comparison with studies reported previously reveals striking similarities in the proposed mechanism.

The activation energy measured by Bywater and Steacie (14) for the ethylene formation from the decomposition of the propyl radical was so low compared to its thermochemical

estimate that a number of studies have been conducted by Calvert and Sleppy (15), Kerr and Trotman-Dickenson (40, 41), Kerr and Calvert (38), and Jackson and McNesby (36) to overcome this descrepancy. They estimated that the proper activation energy value is in the 31 000–37 000 cal/mol range. A comprehensive summary is presented in Table III. Their values also agree with the ones proposed by Heller and Gordon (32).

(b) Post 1960. Back and Takamuku (2) studied the decomposition of photosensitized propane for a temperature range of 300–400 °C. They verified that the decomposition of propyl radicals into propylene had an activation energy of 37 000 cal/mol employing the same mechanism used by Bywater and Steacie (see Table I).

Lin and Laidler (56) sensitized propane by azomethane and studied its decomposition between 250 and 350 °C. Their main objective was to measure the rate of n-propyl radical decomposition. They also proposed a mechanism which contains many termination reactions involving propyl radicals which are quite probable at low temperature range (see Table I).

Papic and Laidler (73) followed this study with an experiment on mercury photosensitized decomposition of propane between 250 and 350 °C. They again concentrated on the decomposition of n-propyl radicals into ethylene and isopropyl radicals into propylene. Their proposed mechanism is an excellent one for low-temperature decomposition of propane at pressures between 2 and 700 Torr. Certain steps have to be added to the mechanism to account for high-pressure reactions. The complete scheme is given in Table II.

Before proceeding to tubular flow reactors, it will be appropriate to mention two other techniques frequently employed by the investigators of propane pyrolysis. Radiolysis and photolysis studies do not present any quantitative data but mostly concern themselves with qualitative discussions of pyrolysis mechanisms. The most recent propane pyrolysis study, which also embraces all others, is presented by Gawlowski (29). The proposed mechanism is presented in Table I. An excellent reference for radiolysis studies on hydrocarbons is the work of Matsuoka (47).

Tubular Flow Reactors

Studies employing tubular flow reactors are usually associated with temperatures at the upper part of medium temperature and the lower part of high-temperature regions (700–1000 °C) and atmospheric pressures. They usually employ advanced gas chromatography techniques; thus they provide an excellent picture of product distributions.

Kunugi et al. (47) studied the pyrolysis of propane for a temperature range of 750–850 °C under ordinary pressure (1 atm) in a transparent quartz tube serving as a reactor. The main products observed were methane, ethylene, hydrogen, propylene, and ethane. Also, C_4 hydrocarbons and heavier products were observed. At low decompositions of propane (less than 20%) the overall reaction may be presented

$$C_3H_8 \rightarrow CH_4 + C_2H_4$$
$$C_3H_8 \rightarrow H_2 + C_3H_6$$
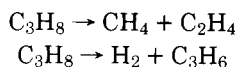
at high decompositions (greater than 40%) propylene further decomposes into ethylene. The decomposition rate was taken as $\frac{3}{2}$ order as proposed by Laidler et al. (49), and A (s^{-1}) was found to be 5.5×10^{13} and E (cal/mol) was found to be 51 500, which was in excellent agreement with literature values (see Tables I and II). The reactions were also carried out in the presence of H_2, N_2, and helium, and their results will be discussed in another section. The mechanism of the decomposition of propane with or without hydrogen is presented in Table I.

Kershenbaum and Martin (43) studied nonisothermal pyrolysis of propane at high temperatures (800–1000 °C). They developed the theoretical basis to determine the order of the reactions and reaction rate constants. Since the flow reactors cannot achieve extremely short residence times as shock tube reactors can, it was necessary to dilute the propane feed with N_2 in order to study the primary kinetics. The overall order of reaction is found to be between 1 and 1.2. The overall rate constant is K (overall) = $2.4 \times 10^{11} \exp(-52\ 100/RT_{max})$ s^{-1}. The mechanism given strictly follows the one proposed by Laidler et al. (49) (see Table II).
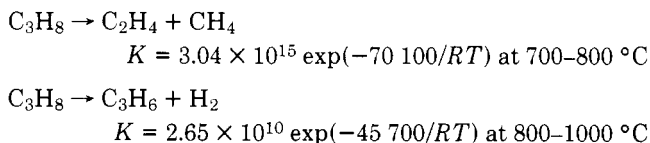
Buekens and Froment (11) studied the thermal cracking of propane in a flow reactor between 625 and 850 °C at atmospheric pressure. They established complete product distributions including those of C_4, C_5, and C_6 and deduced a reaction scheme. They concluded that the activation energy for propane decomposition increases with increasing conversion. A summary of these findings and the reaction scheme are presented in Table I.

Crynes and Albright (17) studied the effects of surface treatments on the pyrolysis of propane between 650 and 750 °C at atmospheric pressures. The rate data show a steady decrease as conversion increases again pointing to an increase in the activation energy. The portions of this study will be reviewed in other sections.

Herriott et al. (33) studied propane pyrolysis with steam and other diluents at temperatures between 700 and 850 °C and at atmospheric pressures. The product distributions were dependent upon steam concentration, surface treatments, temperature, and propane conversion. These aspects will be discussed in other sections of this review. They proposed a mechanism which is presented in Table II.

Kubota (44) estimated the rate equations for a proposed pyrolysis scheme assuming that the rates of initiation and termination reactions were much smaller than those of the propagation reactions. The temperature range was 700–750 °C and the pressure was 1 atm. The mechanism and data are given in Table II.

There are a number of other studies similar to those already mentioned. Kubota et al. (45) proposed an overall reaction mechanism for propane pyrolysis and estimated individual rate constants. Haraguchi et al. (30) described overall reactions as

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$
$$K = 3.04 \times 10^{15} \exp(-70\ 100/RT)\ \text{at } 700\text{–}800\ °C$$

$$C_3H_8 \rightarrow C_3H_6 + H_2$$
$$K = 2.65 \times 10^{10} \exp(-45\ 700/RT)\ \text{at } 800\text{–}1000\ °C$$

and gave the indicated kinetic data. They also stated that the decomposition was first order between 700 and 1000 °C. Finally, Zalotai et al. (103) studied propane pyrolysis at 550 °C.

The Plasma Jet Studies

Complete cracking of hydrocarbons at very high temperatures is achieved in plasma jet experiments. Nishimura et al. (70) studied the effect of hydrogen on the pyrolysis of propane in an induction coupled plasma jet. Propane, highly diluted with argon, was pyrolyzed with hydrogen at temperatures which varied between 10 000 and 12 000 K at the walls of the quartz reactor and between 18 000 and 200 000 K at the center. Carbon, hydrogen, and traces of acetylene are the pyrolysis products. When hydrogen was present, acetylene and ethylene were formed and the amount of soot decreased.

Sato et al. (85) studied propane pyrolysis in a microwave plasma jet at temperatures between 3070 and 9400 °C. The activation energy was 41 400 cal/mol. Mogel and Eremin (67) conducted their experiments in a hydrogen plasma jet and

found that first-order decomposition applies. Finally, Takahashi et al. (*90*) analyzed the plasma jet reactor with the pyrolysis of propane.

The Effect of Other Gases on the Pyrolysis of Propane

(a) **Propane–Propylene Mixtures.** Propane–propylene mixtures were pyrolyzed by Robinson and Weger (*84*) in order to promote butene-1 formation. For zero or very small propylene concentrations the butene-1 concentration was negligible. Conversely, mixtures containing high propylene concentrations promoted butene-1 formation. For a wide range of concentrations the system follows first-order kinetics. At temperatures of 1100 °C and residence times of 1 ms in a quartz flow reactor the initiation steps are

$$C_3H_8 \rightarrow CH_3 \cdot + C_2H_5 \cdot$$
$$C_3H_6 \rightarrow C_3H_5 \cdot + H \cdot$$
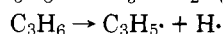
Also, it was determined that propane accelerated the decomposition of propylene.

Haraguchi et al. (*31*) proposed rate constants of propane and propylene pyrolysis for mixtures of various proportions of these hydrocarbons. They studied the system at 820 to 940 °C. Propane accelerated the propylene decomposition evidenced by a decrease in E (C_3H_6) from 60 700 to 52 800 cal/mol for increasing (0–100%) propane concentrations. Also, A (C_3H_6) (s^{-1}) decreased from 1.27×10^{12} to 3.17×10^{11}. On the other hand, for increasing propylene concentrations (0–100%) in propane, E (C_3H_8) increased from 58 900 to 101 000 cal/mol and A (C_3H_8) (s^{-1}) from 1.46×10^{12} to 1.01×10^{20}, indicating an inhibiting effect from propylene.

Kershenbaum and Martin (*43*) studied the effect of propylene on the decomposition of propane to analyze the self-inhibition of propane. Propylene showed a marked effect on the inhibition of propane decomposition.

(b) **Other Mixtures.** (i) **Inerts.** Since Pease and Durgan (*77*) illustrated that inerts such as He, Ar, N_2, etc. do not affect the reaction rates of propane decomposition, these substances are freely used to achieve low propane concentrations in feeds and to ensure low conversions. Also, Laidler et al. (*49*) demonstrated that CO_2 had no effect on these reactions.

(ii) **Others and Treatments.** The effect of O_2 was most extensively studied by Leathard and Purnell (*53*), Martin et al. (*61*), and Crynes and Albright (*17*). Oxygen greatly accelerated the reaction if the vessel was unpacked. At high S/V ratios O_2 decelerated the reaction rates. When the reactor was pretreated, the acceleratory effect of O_2 was intensified except PbO and KCl pretreatment increased the deceleratory effect in reactors with high S/V ratios. Benson (*3*) determined that 0.2% O_2 in Ar had no effect on the selectivity pattern of pyrolysis products.

Kunugi et al. (*47*) determined that hydrogen accelerates the decomposition of propane. It also increases the selectivity of the formation of methane and ethane. Crynes and Albright determined that an H_2 treatment following an O_2 treatment reduced the accelerating effect of the O_2 treatment by deactivating the walls.

H_2S effects on the pyrolysis of propane were studied by Benson (*51*) and Crynes and Albright (*17*). The former determined that H_2S maintains the propylene selectivity which usually decreases as ethylene selectivity increases. Also, H_2S enhanced methane formation at the expense of ethane. The latter showed that an H_2S treatment deactivated the walls of the reactor treated by O_2 previously. It may be concluded at this point that H_2S and H_2 act similarly when they are introduced into an O_2 treated reactor.

Nitric oxide effects were investigated by Martin et al. (*61*) and Laidler et al. (*50*). They determined that NO inhibited the reaction and for high S/V ratios this effect was more pronounced. Crynes and Albright (*17*), on the other hand, report no effect of NO treatment on the rate of reactions.

The effects of steam were investigated by Martin et al. (*61*), Crynes and Albright (*17*), and Herriott et al. (*33*). Both Martin and Crynes reported that steam accelerated propane decomposition though not as effectively as O_2. Herriott used H_2S and steam to show that H_2S indeed prevents the activating role of steam as claimed by Crynes. Crynes and Albright (*17*) also used HBr treatment. It exhibited a wall activity, however, not so high as in O_2 treated reactors.

(iii) **Miscellaneous Mixtures.** Shirotsuka et al. (*87*) examined the pyrolysis of propane and n-pentane in a shock tube reactor for a temperature range of greater than 727 °C. They determined that the rate constants and activation energy values reported for other temperature ranges do not apply above 1027 °C.

Martin et al. (*62*) reported the following data for the co-pyrolysis of propane and isopentane at 550 °C in a static system at 25 mmHg;

$$C_3H_8 \rightarrow H_2 + C_3H_6 \text{ (first order)}$$
$$C_3H_8 \rightarrow CH_4 + C_2H_4 \text{ (first order)}$$
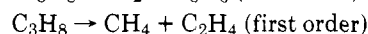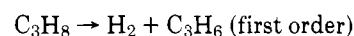
while both reactions were second order if O_2 was added to the system.

Blanchet and Parent (*7*) determined that propane pyrolysis reactions in the presence of vapor phase graphite at 1700–4700 °C can be represented as

$$2C_3H_8 \rightarrow 3C_2H_2 + 5H_2$$
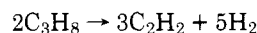
Menbus (*65*) studied the pyrolysis of propane in an argon plasma jet with the presence of Al vapor and tungsten particles. The acetylene yield was 93% at 3700–4700 °C.

Keneshea et al. (*37*) showed that the products from the propane pyrolysis over molten salts were C_3H_6, C_2H_6, C_2H_4, CH_4, H_2, butanes, and higher hydrocarbons. Increasing propane conversion (10–90%) decreased propylene selectivity (25–10%).

Finally, Beyer et al. (*5*) studied the catalytic decomposition of propane over decationized clinoptilolite. The overall decomposition was first order and the activation energy was greatly reduced by the catalyst from the usual range of 55 000–68 000 cal/mol to 33 700 cal/mol.

Surface Effects

Certain reactor walls are very effective in promoting the secondary reactions of propylene and ethylene during propane pyrolysis. The reactor walls undoubtedly have a role in the free-radical chain initiation and termination reactions of propane pyrolysis; however, these effects are more subtle and under the conditions of the experiments reviewed, their influence cannot be determined precisely.

(a) **S/V (Surface to Volume Ratio).** Pease and Durgan (*77*) conducted pioneering work in this field and concluded that to change the (S/V) does not affect the propane pyrolysis at 650 °C. Voevodsky (*99*) presented evidence that a tenfold (1.1–12 cm^{-1}) increase in S/V reduced the rate of propane pyrolysis in a quartz reactor at 610 °C. Laidler et al. (*49*) substantiated this finding by observing a reduction in the reaction rate in a quartz reactor at 580 °C. The rate fell by 35% when (S/V) was increased 12-fold. But Martin et al. (*61*) and Leathard and Purnell (*53*) showed that this effect was the influence of oxygen which could not be detected and at high (S/V) acted as an inhibitor. They found no dependence of the reaction rate on (S/V) for a temperature range of 510–560 °C and (S/V) from 0.7 to 16 cm^{-1}. Also, Martin et al. (*60*) and Leathard and Purnell (*52*) have stated in quartz, Pyrex, Pyrex coated with KCl, Pyrex treated with chromic acid, HF, and PbO, and in untreated vessels no changes were observed in the

rate of pyrolysis, with a change in (S/V). Crynes and Albright (17) observed no rate changes when S/V was increased by a factor of 2.6 during the pyrolysis of propane at 750 °C.

(b) The Role of Surfaces. At low temperatures and pressures, however, increasing the S/V ratio may affect the rate of propane decomposition. Leathard and Purnell (52) reported an unusual reduction in the rate of the pyrolysis of propane of about 450 °C and at 20 mmHg. The rate fell about 50% when (S/V) was increased from 0.9 to 6.3 cm^{-1}. Niclause (68) also reported a weak inhibitory surface effect at 500 °C. This kind of heterogeneous behavior was attributed to the deactivation of hydrogen radicals behavior at the walls. Since the energy of this process is less than 13 000 cal, it is likely to happen at low temperatures and may lead to inhibition since this reaction will dominate the chain termination steps. Crynes and Albright (17) found that nickel, stainless steel, and low-carbon steel reactors give similar results. However, the formation of a carbon layer during pyrolysis in the low-carbon steel reactors made these reactors unsuitable for comparison since carbon coatings are, in fact, highly reactive. Finally, Tamai et al. (91) investigated propane pyrolysis in gold, iron, and quartz reactors. The decomposition rate of propane varied greatly and it was considered that the walls affected radical chain reactions at initiation and termination.

Summation and Interpretation

An overall examination of Tables I, II, and III reveals that there has been considerable interest and research on propane pyrolysis in recent years. The propane pyrolysis mechanism is one of the best understood among lower hydrocarbons. The main problems, such as conversion, pressure, and temperature dependency of activation energies and rate constants, the effect of self-inhibitions, and the effect of isomerizations are largely understood. The element which creates confusion among researchers is the fact that it is difficult to duplicate experiments to substantiate or refute different proposals for mechanisms and other kinetic data.

(a) Operating Conditions. Most of the studies presented deal with the low-temperature and medium-temperature regions employing static and tubular flow reactors respectively (25–750 °C). High-temperature studies use the shock tube. The advantage of the latter is that it permits the study of the reaction at high temperatures near to or at practical commercial levels. In the flow and conventional reactors it would be impossible to gather data about the reactions at high temperatures since the products of the pyrolysis themselves would decompose thus preventing the detection of the early product distribution by a gas chromatograph. In the shock tube the residence times may be as short as 0.1 ms which gives an excellent opportunity for the study of the initial pyrolysis reactions and products. Although many experiments employ atmospheric pressures, some studies were conducted in very low pressure ranges such as 2 mmHg.

(b) Reaction Mechanisms. In formulating a reaction mechanism it is often helpful to have experimental data describing rate constants and identifying possible reaction products. Another important source of data obtained from a review of the literature or from thermochemistry is the relative importance of the steps proposed for propane pyrolysis. Undoubtedly the decomposition of isopropyl radicals into ethylene is much slower than its decomposition into propylene, and for the n-propyl radicals the opposite is true. Also, one has to account for self-inhibition which usually exhibits itself by the combination of H· radicals with ethylene and propylene, thus decreasing the propagation rate of the decomposition. Finally, when the rate constants resulting from the simulation of the mechanism are compared to the thermochemical and literature data, one expects a match.

A quick examination of Table III reveals that there is no

individual value of the Arrhenius parameter and activation energy for a reaction step; rather, ranges of values are found. This situation results from many factors. One is the difficulty of determining simultaneously several parameters from experimental data. As decreasing activation energy with increasing temperature points out, the mechanism of propane pyrolysis at high temperatures becomes more complex. Also, it may indicate that the experiment is performed under conditions limited by heat transfer. In addition, most of these values are derived by low-temperature experiments and the extrapolation of these values to high temperatures may produce incorrect results. Another source of error is the neglect by many researchers to include the reverse reactions of usually accepted initiation and propagation steps while working at medium or low temperatures and at low conversions. Many intermediate steps which were not included in the low temperature reaction mechanism became important at high temperatures. The inclusion of these free radical steps into the mechanism changes the final form of the rate equation which will invariably be obtained by steady-state approximation. Thus, it is not surprising to find out that the overall rate of propane decomposition represented by a complex equation will deviate from first-order kinetics as postulated by many investigators. The increase in the order due to the complexities introduced into the rate equation at high temperatures also explains the different value of activation energy (55 000 rather than 67 000 cal/mol) found in high temperature studies.

Even though various papers propose different values of Arrhenius parameters and activation energies for the same initiation, propagation and termination reactions included in propane pyrolysis mechanisms, there are a number of experiments which are exhaustive in their studies of the subject and can be considered more reliable than other works. In the low-temperature range (25–400 °C) Papic and Laidler (73) and Lin and Laidler (56) and in the medium-temperature range (400–800 °C) Leathard and Purnell (52, 53) and Laidler et al. (49) employing a static system arrived at similar results. Likewise, Kershenbaum and Martin (43), Buekens and Froment (11), Kunugi et al. (47), and Kubota (44) employing the tubular flow system reached the same conclusions about product distributions, overall order, and activation energy of propane pyrolysis in the medium–high-temperature range (700–1000 °C). The studies of Lifshitz and Frenklach (54) employing the shock tube and Van Damme et al. (98), employing a pilot plant should also be given appropriate attention. In the area of the effect of surfaces on propane pyrolysis, the works of Martin et al. (60) and Crynes and Albright (17) should be considered while the works of Robinson and Weger (84) and Haraguchi et al. (31) are representative in the area of the pyrolysis of propane–propylene mixtures.

The following observations can be synthesized from these works. (1) Propane pyrolysis follows first-order kinetics (overall) when the decomposition rate of propane is low (0–10%) and residence time in the reactor is short (~1 s). Under these conditions the rate equation can be represented by 10^{12} exp($-55\ 000/RT$). (2) As the decomposition rate of propane varies from 10 to 90% and the residence time in the reactor is long (in minutes), propane pyrolysis has $3/2$-order overall kinetics and the rate equation can be represented by 10^{14} exp($-67\ 000/RT$). (3) Although the propriety of including other steps for temperature and pressure ranges not covered by these studies should be considered, Table V illustrates a kinetic model proposed for the pyrolysis of propane.

(c) Product Distribution and Selectivity. The major products of propane pyrolysis are H_2, CH_4, C_2H_4, and C_3H_6. C_2H_6 is an important product followed by C_4 and C_5+ hydrocarbons. Van Damme et al. (98), Herriott et al. (33), and

Table V. Comprehensive Kinetic Model and Rate Data for the Pyrolysis of Propane

Reaction	A (s^{-1})	E (cal/mol)
$C_3H_8 \rightarrow CH_3\cdot + C_2H_5\cdot$	4×10^{17}	82 000
$C_3H_8 \rightarrow H\cdot + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot$	10^{17}	98 000
$CH_3\cdot + C_3H_8 \rightarrow CH_4 + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot$		
$C_2H_5\cdot + C_3H_8 \rightarrow C_2H_6 + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot$	4×10^{11}	10 000
$H\cdot + C_3H_8 \rightarrow H_2 + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot$	10^{14}	8 200
$n\text{-}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4$	10^{14}	32 000
$n\text{-}C_3H_7\cdot \rightarrow H\cdot + C_3H_6$[a]	10^{14}	38 000
$i\text{-}C_3H_7\cdot \rightarrow H\cdot + C_3H_6$	10^{14}	40 000
$i\text{-}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_4$[a]	5×10^{11}	32 000
$CH_3\cdot + C_3H_6 \rightarrow CH_4 + C_3H_5\cdot$	6×10^{10}	7 500
$H\cdot + C_3H_6 \rightarrow \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot$	10^{12}	3 000
$H\cdot + C_3H_6 \rightarrow H_2 + C_3H_5\cdot$	10^{11}	1 500
$H\cdot + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot \rightarrow CH_3\cdot + C_2H_5\cdot$	10^{14}	
$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot$	10^{11}	5 000
$C_2H_5\cdot \rightarrow H\cdot + C_2H_4$	10^{14}	40 000
$C_3H_5\cdot + C_3H_6 \rightarrow C_6H_{10} + H\cdot$	10^9	15 000
$2n\text{-}C_3H_7\cdot \rightarrow n\text{-}C_6H_{14}$[b]	10^{14}	
$2i\text{-}C_3H_7\cdot \rightarrow 2,3\text{-dimethylbutane}$	10^{14}	
$2n\text{-}C_3H_7\cdot \rightarrow C_3H_8 + C_3H_6$	10^{13}	
$2i\text{-}C_3H_7\cdot \rightarrow C_3H_8 + C_3H_6$	10^{13}	
$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$	10^{14}	
$CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8$	10^{11}	
$CH_3\cdot + C_3H_5\cdot \rightarrow C_4H_8$	5×10^{10}	
$CH_3\cdot + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot \rightarrow C_3H_6 + CH_4$	10^{14}	
$CH_3\cdot + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot \rightarrow C_4H_{10}$	10^{14}	
$H\cdot + \genfrac{}{}{0pt}{}{i\text{-}}{n\text{-}}C_3H_7\cdot \rightarrow C_3H_8$	10^{15}	

[a] Less likely to take place. [b] Negligible at high temperatures.

Buekens and Froment (11) gave extensive data on product distributions and selectivities. Selectivity of a particular product is defined as the weight of product formed per weight of propane cracked. As the conversion of propane increases, the selectivities of CH_4 and C_2H_4 increase, the selectivity of H_2 remains the same, while the selectivity of C_3H_6 decreases. This is attributed to the fact that C_3H_6 combines with $H\cdot$ radicals to form $i\text{-}C_3H_7\cdot$ which isomerizes into $n\text{-}C_3H_7\cdot$ which, in turn decomposes into C_2H_4 and $CH_3\cdot$. Increased $CH_3\cdot$ concentration leads to the formation of ethane whose selectivity increases as propane conversion increases.

Low total pressure and low propane partial pressure decreases the propane conversion requiring possible reconcentration of the unreacted feedstock. This situation may be desirable since C_3H_6 production will be kept at high levels while the H_2, CH_4, C_3H_6 production will not be affected. Propylene addition decreases the partial pressure of propane, and thus decreases propane conversion. Also it inhibits the propane decomposition by lowering $H\cdot$ concentration as discussed in the above paragraph.

(d) Order of the Reaction and Activation Energy. Early

experiments indicated first-order kinetics whereas almost all of the studies after 1965 point to an overall order between 1.0 and 1.5. Laidler et al. (49) gave an explanation to this phenomenon by pointing out that at high or medium temperatures and low pressures the order becomes 1.5. This also explains the results of the overall activation energy reports which are clustered around 56 000 and 67 000 cal/mol. Indeed, Laidler et al. calculated it to be 55 000 cal/mol at the $\frac{3}{2}$-order region and 67 000 at the first-order region. It is not surprising that simple order kinetic equations do not apply. The complexity of the reaction mechanism prevents such a simplistic approach.

(e) Arrhenius Parameters. The evaluation of Arrhenius parameters requires first a knowledge of the parameters for initiation and termination reactions and secondly, correct elucidation of the overall rate parameters corresponding to the initial reaction. Thus, the problem is twofold. First, the uncertainty about the parameters of the inhibition and termination reactions, whether directly measured or estimated, lies within a factor of 100. Indeed, an evaluation of the data about the combination of 2-methyl radicals will illustrate the point. If we realize that this termination reaction is the most important chain ending step in propane pyrolysis, the problem becomes apparent. Of much greater importance is the difficulty of evaluating true, overall initial rate parameters. The oversimplified rate equations, invalid steady-state approximation assumptions, incorrect mechanisms, undetected and unaccounted for impurities, and isomerization and self-inhibition reactions all contribute to this problem. This explains in part the variability in the magnitude of the parameters describing the various propagation steps in Tables II and III.

(f) Role of Surfaces. At or near the operating conditions of industry, surface effects do not play an important role in propane decomposition as long as no impurities, notably oxygen, are present in the reaction system. At low temperatures, however, wall activity plays an important role in the decrease of the decomposition rate by destroying $H\cdot$ radicals which are very important chain carriers.

Conclusions

Numerous articles reviewed in this study state that propane pyrolysis has an overall reaction order of one (13, 49, 82), while others (60, 53, 11, 47, 43) propose orders between 1.0 and 1.5. The overall rate parameters calculated in these studies also differ. Arrhenius constants fall between 10^{11} and 10^{14} s^{-1} while activation energies vary from 51 000 to 68 000 cal/mol. These differences are explained by noting that the temperature and pressure levels and the extents of propane conversion employed in these experiments are different (see Tables I and II). Other studies explored the effect of propylene (84, 31, 43), inerts (77, 49), oxygen (53, 61, 17, 3), hydrogen (47, 17), hydrogen sulfide (3, 17), nitric oxide (61, 50, 17), and steam (61, 17, 33) on the pyrolysis of propane. Propylene, oxygen, and NO were found to inhibit propane pyrolysis. Inerts did not affect the decomposition of propane, while hydrogen, H_2S, and steam accelerated it. Finally, a few studies were conducted on the heterogeneous pyrolysis of propane (7, 65, 37, 5) which showed that the decomposition was accelerated in the presence of solids.

The effect of varying the surface to volume ratio (S/V) was also studied by many researchers (99, 49, 61, 53, 60, 17). It was determined that (S/V) did not affect the decomposition of propane while it was shown that different surfaces (52, 68, 17, 91) such as gold, nickel, carbon steel, stainless steel, and quartz affected the order and the activation energy of propane decomposition.

It is clear under the light of recent experiments that the conventional quartz reactor, which served as a basis for several

studies and gave badly needed information about propane pyrolysis, is not suitable for studies conducted in high (greater than 800 °C) temperature regions. The residence time in static reactors is high (minutes) which invariably results in the loss of many pyrolysis products which if not observed prevent the construction of an accurate pyrolysis mechanism. The shock tubes and the tubular flow reactors have the ability to restrict the residence times of the reaction mixtures to less than 0.1 ms (54, 44, 33, 3, 47, 43, 11, 17, 45, 30, 103). As a result the immediate products of the propane pyrolysis can be observed and an accurate mechanism can be proposed. Also, studies at high-temperature regions are desirable since these temperature levels are employed by the petrochemical industry. Finally, studies at the plant level (98, 21) produce data which can be directly used in industrial operations.

It is important to stress the areas of agreement rather than the discrepancies in the field of propane pyrolysis. The mechanism of propane pyrolysis is more or less agreed upon. The importance of certain steps at particular temperatures is also an accepted fact. As noted before, the most important steps in the development of kinetic data and mechanisms are: (a) the determination of the products which is becoming increasingly effective by the introduction and application of better techniques; (b) the construction of a mechanism which will qualitatively predict the existence of these products which will not be grossly contradictory to the previous experiments and thermochemical facts; (c) the evaluation of overall rate data and simulation of the mechanism. This step necessarily requires a computer program and a tight control of impurities such as oxygen which was shown to interfere with propane pyrolysis to a great extent. Programs, such as RRKM (Rice–Ramsperger–Kassel–Marcus) and the general mechanism proposed by Bradley and his co-workers (15, 23) will play an important role; (d) the determination of optimum rate constants such that they will reproduce the experimentally observed product distribution.

Since the basic divisions of opinion have disappeared and the technical advances have established the ability of different laboratories to reproduce each other's information closely, it will be proper to suggest that future publications should present their results in such a way that the raw data can be generated for comparison. If the experiments are conducted with the above steps in mind, the details of propane pyrolysis will be further understood during the next few years. One more step necessary in this direction will be the abandonment of the steady-state theory to some extent. Of course, this approach promises great difficulty, but the construction of pyrolysis computer programs for universal use offers some easing of the problem.

The recent trends in the experimental studies of propane pyrolysis are pointing to the fact that these investigations are being conducted under circumstances near industrial operating conditions. This fact does not decrease at all the importance of any experiment which was conducted under laboratory conditions. Indeed, the latter form the backbone of our knowledge of propane pyrolysis.

Literature Cited

(1) Amano, A., Uchiyama, M., J. Phys. Chem., **67**, 1242 (1963).
(2) Back, R. A., Takanuku, S., J. Am. Chem. Soc., **86**, 2558 (1964).
(3) Benson, A. M., AIChE J., **13**, 903 (1967).
(4) Benson, S. W., O'Neal, H. E., Natl. Bur. Stand., Ref. Data Ser., No. 21 (1970).
(5) Beyer, H., et al., Rev. Roum. Chim., **17**, 29 (1972).
(6) Blakemore, J. E., Corcoran, W. H., Ind. Eng. Chem., Process Des. Dev., **8**, 206 (1969).
(7) Blanchet, J. L., Parent, J. R., Can. J. Chem. Eng., **45**, 361 (1967).
(8) Bradley, J. N., Proc. Roy. Soc., Ser. A, **337**, 199 (1974).
(9) Bradley, J. N., Frend, M. A., J. Phys. Chem., **75**, 1492 (1971).
(10) Bradley, J. N., West, K. O., Trans. Faraday Soc. I, **72**, 8 (1976).
(11) Buekens, A. C., Froment, G. F., Ind. Eng. Chem., Process Des. Dev., **7**, 435

(1968).
(12) Bull, K. R., et al., Proc. Roy. Soc., Ser. A, **342**, 259 (1975).
(13) Bull, K. R., et al., J. Chem. Soc., Faraday I, **64**, 405 (1968).
(14) Bywater, S., Steacie, E. W. R., J. Chem. Phys., **19**, 319 (1951).
(15) Calvert, J. G., Sleppy, W. C., J. Am. Chem. Soc., **81**, 1544 (1959).
(16) Clark, T. C., et al., J. Chem. Phys., **54**, 1295 (1971).
(17) Crynes, B. L., Albright, L. F., Ind. Eng. Chem., Process Des. Dev., **8**, 25 (1969).
(18) Cvetanevic, R. J., Irvin, R. S., J. Chem. Phys., **46**, 1694 (1967).
(19) Darwent, de B. B., Roberts, R., Discuss. Faraday Soc., **14**, 55 (1953).
(20) Darwent, de B. B., Steacie, E. W. R., J. Chem. Phys., **13**, 563 (1945).
(21) Davis, H. G., Farrell, T. J., Ind. Eng. Chem., Process Des. Dev., **12**, 171 (1973).
(22) Dintess, A. I., Frost, A. V., R. Acad. Sci. (USSR), **5**, 513 (1934).
(23) Dintess, A. I., Frost, A. V., R. Acad. Sci. (USSR), **4**, 153 (1933).
(24) Dintess, A. I., Frost, A. V., J. Gen. Chem. (USSR), **3**, 747 (1933).
(25) Eltenton, G. C., J. Chem. Phys., **15**, 455 (1947).
(26) Fedeseev, S. D., Artamanov, E. V., Kinet. Katal., **11** (5), 1102 (1970).
(27) Frey, H. M., Hepp, H. J., Ind. Eng. Chem., **25**, 441 (1933).
(28) Frey, H. M., Walsh, R., Chem. Rev., **69**, 103 (1969).
(29) Gawlowski, J., Can. J. Chem., **53**, 1348 (1974).
(30) Haraguchi, T., et al., Kagaku Kogaku, **33** (8), 786 (1969).
(31) Haraguchi, T., et al., Int. Chem. Eng., **16**, 354 (1974).
(32) Heller, C. A., Gordon, A. S., J. Phys. Chem., **62**, 709 (1958).
(33) Herriott, G. E., et al., AIChE J., **18**, 84 (1972).
(34) Hobbs, J. E., Hinshelwood, C. N., Proc. Roy. Soc., Ser. A, **167**, 447 (1938).
(35) Ingold, K. U., et al., Proc. Roy. Soc., Ser. A, **203**, 486 (1950).
(36) Jackson, W. M., McNesby, J. R., J. Am. Chem. Soc., **83**, 4891 (1961).
(37) Keneshea, F. J., et al., Ind. Eng. Chem., Prod. Res. Dev., **10**, 25 (1971).
(38) Kerr, J. A., Calvert, J. G., J. Am. Chem. Soc., **83**, 3391 (1961).
(39) Kerr, J. A., Personage, M. J., "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworth, London, 1972.
(40) Kerr, J. A., Trotman-Dickenson, A. F., Trans. Faraday Soc., **55**, 572 (1959).
(41) Kerr, J. A., Trotman-Dickenson, A. F., Trans. Faraday Soc., **55**, 921 (1959).
(42) Kinoshito, H., Shibatani, H., Int. Chem. Eng., **14**, 173 (1974).
(43) Kershenbaum, L. S., Martin, J. J., AIChE J., **13**, 148 (1967).
(44) Kubota, K., J. Chem. Soc. Jap., Ind. Chem. Sect., No. 8, 1393 (1974).
(45) Kubota, K., Morita, N., Kagaku Kogaku, **34** (6), 612 (1970).
(46) Kunugi, T., et al., Ind. Eng. Chem., Fundam., **9**, 319 (1970).
(47) Kunugi, T., et al., Ind. Chem. Eng., **7**, 550 (1967).
(48) Kuppermann, A., Larson, J. G., J. Chem. Phys., **33**, 1264 (1960).
(49) Laidler, K. J., et al., Proc. Roy. Soc., Ser. A, **270**, 242 (1962).
(50) Laidler, K. J., et al., Proc. Roy. Soc., Ser. A, **270**, 254 (1962).
(51) Laidler, K. J., Wojciechowski, B. W., Proc. Roy. Soc., Ser. A, **259**, 257 (1960).
(52) Leathard, D. A., Purnell, J. H., Proc. Roy. Soc., Ser. A, **306**, 553 (1968).
(53) Leathard, D. A., Purnell, J. H., Proc. Roy. Soc., Ser. A, **305**, 517 (1968).
(54) Lifshitz, A., Frenklach, M., J. Phys. Chem., **79**, 686 (1975).
(55) Lin, M. C., Back, M. H., Can. J. Chem., **44**, 2369 (1966).
(56) Lin, M. C., Laidler, K. J., Can. J. Chem., **44**, 2927 (1966).
(57) Lin, M. C., Laidler, K. J., J. Chem. Soc., Faraday I, **64**, 79 (1968).
(58) Marek, L. F., McCluer, W. B., Ind. Eng. Chem., **23**, 878 (1933).
(59) Martin, R., et al., R. Acad. Sci., Ser. C, 254 (1962); 1786 (1962).
(60) Martin, R., et al., J. Chem. Phys., **61**, 286 (1964).
(61) Martin, R., et al., J. Chem. Phys., **61**, 790 (1964).
(62) Martin, R., et al., Can. J. Chem., **43**, 1120 (1965).
(63) Martin, R., et al., Can. J. Chem., **43**, 1120 (1965).
(64) Mellotte, H., et al., Bull. Soc. Chem., 2562 (1969).
(65) Menbus, P., Can. J. Chem. Eng., **53**, 653 (1975).
(66) Metcalfe, E. L., Trotman-Dickenson, A. F., J. Chem. Soc., 4620 (1962).
(67) Mogel, G., Eremin, E. N., Zh. Fiz. Khim., **44** (1), 43 (1970).
(68) Niclause, M., Bull. Soc. Chem., 1599 (1968).
(69) Niclause, M., et al., Ind. Chim. Belge, **32**, 674 (1967).
(70) Nishimura, Y., et al., Int. Chem. Eng., **10**, 133 (1970).
(71) Pacey, P. D., Purnell, J. H., Int. J. Chem. Kinet., **4** (6), 657 (1972).
(72) Pacey, P. D., Purnell, J. H., Ind. Eng. Chem., Fundam., **11**, 233 (1972).
(73) Papic, M. M., Laidler, J. K., Can. J. Chem., **49**, 535, 549 (1971).
(74) Papic, M. M., Laidler, J. J., Can. J. Chem., **49**, 549 (1971).
(75) Paul, R. E., Marek, L. F., Ind. Eng. Chem., **26**, 454 (1934).
(76) Pease, R. N., J. Am. Chem. Soc., **50**, 1779 (1928).
(77) Pease, R. N., Durgan, E. S., J. Am. Chem. Soc., **52**, 1262 (1930).
(78) Powers, O. R., Corcoran, W. H., Ind. Eng. Chem., Fundam., **13**, 351 (1974).
(79) Purnell, J. H., Quinn, C. P., Nature (London), **189**, 656 (1961).
(80) Purnell, J. H., Quinn, C. P., Ed., "Photochemistry and Reaction Kinetics", Cambridge University Press, 1966.
(81) Purnell, J. H., Quinn, C. P., Proc. Roy. Soc., Ser. A, **270**, 267 (1967).
(82) Rice, F. O., J. Am. Chem. Soc., **53**, 1959 (1931).
(83) Rice, F. O., Herzfeld, K. R., J. Am. Chem. Soc., **56**, 284 (1934).
(84) Robinson, K. K., Weger, E., Ind. Eng. Chem., Fundam., **10**, 198 (1971).
(85) Sato, K., et al., J. Chem. Soc. Jap., Ind. Chem. Sect., 7257 (1974).
(86) Shibatani, H., Konoshita, H., J. Chem. Soc. Jap., Ind. Chem. Sect., 342 (1973).
(87) Shirotsuka, T., Kagaku Kogaku, **33** (1), 121 (1969).
(88) Steacie, E. W. R., Dewar, D. J., J. Chem. Phys., **8**, 571 (1949).
(89) Steacie, E. W. R., Puddington, I. E., Can. J. Res., Sect. B, **16**, 176 (1938).
(90) Takahashi, T., Kagaku Kogaku, **35** (4), 429 (1971).
(91) Tamai, Y., et al., Hokuku Univ. J., **15**, 255 (1969).
(92) Trotman-Dickenson, A. F., Am. Rep. Chem. Soc., 36 (1968).
(93) Trotman-Dickenson, A. F., Advan. Free-Radical Chem., **1**, 1 (1965).
(94) Trotman-Dickenson, A. F., Kerr, J. A., "Progress in Reaction Kinetics", Vol. L, G. Porter, Ed., Pergamon Press, London, 1961.

(95) Trotman-Dickenson, A. F., Steacie, E. W. R., *J. Chem. Phys.*, **19**, 169 (1951).
(96) Trotman-Dickenson, A. F., Milne, G. S., *Nat. Bur. Stand., Ref. Data Ser. No. 9*, 108 (1967).
(97) Truby, F. K., Rice, J. K., *Int. J. Chem. Kinet.*, **V**, 721 (1973).
(98) Van Damme, P., et al., *AIChE J.*, **21**, (1975).
(99) Voevodsky, V. V., *Trans. Faraday Soc.*, **55**, 65 (1959).
(100) Voevodsky, V. V., Kondratiev, V. N., "Progress in Reaction Kinetics", Vol. III, G. Porter, Ed., Pergamon Press, London (1961).
(101) Wang, Y. L., et al., *Ind. Eng. Chem., Fundam.*, **2**, 161 (1963).
(102) Yang, K. A., *J. Am. Chem. Soc.*, **84**, 719 (1962).
(103) Zalotai, L., et al., *Int. Chem. Eng.*, **10**, 133 (1970).

The Removal of Emulsified Oil Particles from Water by Flotation

Christina Angelidou, Elaheh Keshavarz, M. J. Richardson, and G. J. Jameson*

Department of Chemical Engineering, Imperial College, London, S.W.7, England

The flotation of emulsified oil particles suspended in low concentrations in water has been studied. Two oils were used: a spontaneously emulsifying cutting oil or machining lubricant, and white spirit, a petroleum based turpentine substitute which was emulsified by intense agitation. The oil concentrations were up to 200 mg/L. To effect the separation, various cationic surfactants were used in the flotation cell which was operated batchwise with an external total recycle. It was found that the rate of flotation in water increased with addition of surfactant up to a limit. The presence of sea salt reduced the flotation rate. Simple mathematical models of the flotation cell are developed for predicting the flotation rate from first principles. The agreement between predicted and measured flotation rates is quite good.

Introduction

Oil–water separation techniques have gained increasing attention in recent years because of the need for treating oil-polluted waste waters. Oil–water emulsions are found in waste water effluent streams from many sources, including petroleum refineries (Steck, 1966; Quigley, 1966), the discharge of bilge and ballast water from ships (Hernandez et al., 1966), washrack and hanger waste waters, rolling mills, and chemical processing and manufacturing plants. Many commercial techniques and devices are being developed and marketed for the removal of emulsified oil from water, but a single, economical, and efficient method is not yet available (Wang et al., 1975).

Flotation, one of the adsorptive bubble separation techniques (Karger et al., 1967; Lemlich, 1972), being basically a large-scale process offers a great deal of potential for the treatment of sewage and industrial wastes (Grieves, 1970; Boyd and Shell, 1972; Jenkins et al., 1972). Air flotation applied to the separation of emulsified oil from water involves the injection of fine air bubbles on which oil agglomerates or oil drops adhere in the presence of a surface-active agent (or surfactant) and are removed by rising to the water surface and being trapped into the resulting foam which is subsequently removed (*Effluent Water Treat. J.*, 1969; Rohlich, 1954; Barry, 1951).

In dispersed-air flotation, air bubbles are generated either by electrolysis or by forcing air through a spinnerette, porous glass frit, single orifice, or other suitable sparger. Small bubbles of diameters less than 0.1 mm can be produced electrolytically but the bubble size distributions obtained in this way are not reproducible (Reay and Ratcliff, 1975). The size distributions of bubbles produced by spargers are governed mainly by the size distribution of the sparger pores and the air flow rate (Shah and Lemlich, 1970). Small bubbles with reproducible size distribution can be generated on a porous glass frit by adding up to 0.5 vol % of a frother (a short chain aliphatic alcohol) to the solution (Zieminski et al., 1967; Reay and Ratcliff, 1975), although for economic reasons such alcohol addition would not be practicable on the large scale.

Effluent treatment flotation plants tend to use small bubbles often of diameter less than 0.1 mm (Reay and Ratcliff, 1973) which distinguishes this process from the froth flotation process used for many years in mineral dressing. A theoretical analysis exploring the effect of bubble size on flotation rate in dispersed-air operation, supported by experimental confirmation (Reay and Ratcliff, 1973, 1975), has shown that for small bubbles of diameter up to 0.1 mm around which Stokes flow can be applied, the flotation rate should, to a first approximation, be proportional to bubble frequency and be independent of bubble diameter over a range of particle sizes (up to 20 μm in diameter) often encountered in effluent streams. Therefore for a given air rate the bubbles should be made as small as possible in order to maximize their frequency. Of course, this must be balanced against the extra cost of generating smaller bubbles in the case of spargers and porous plates, the method of electrolysis being left to date as the main alternative for industrial applications (Kuhn, 1974; *Water Waste Treat. J.*, 1968). Because of the dependence of the flotation rate on the bubble size, it is clear that a need exists to produce small gas bubbles of controllable and predetermined size, by an economical process.

Most of the work on effluent flotation has dealt with the chemical aspects of the process and very little work has been done on the physics of bubble–particle attachment. Collins and Jameson (1976, 1977) recently conducted an experimental investigation on the physical variables that control the kinetics of the flotation of fine particles by small bubbles of diameters less than 0.1 mm, stimulated in part by a suggestion made by Reay and Ratcliff (1975), and showed that the rate of flotation depends strongly on the double layer repulsion between par-