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Investigation of the Bromination/Dehydrobromination of Long Chain Alkanes

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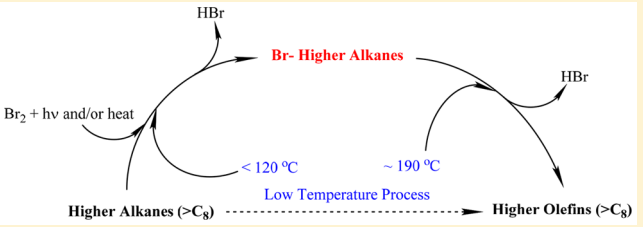
ABSTRACT: The partial oxidation of dodecane and paraffin wax with bromine at relatively low temperatures (≤120 °C) and the dehydrobromination of the subsequent alkyl bromide intermediates at higher temperatures (>175 °C) to form higher alkenes were investigated. Products were analyzed using nuclear magnetic resonance spectroscopy, gas chromatography, and mass spectrometry. Bromination favored the formation of alkyl bromides on internal carbons of the model long chain alkanes over terminal sites. At lower temperatures (~90 °C), ultraviolet photochemical initiation of bromination was necessary, while above 105 °C, thermally initiated bromination was observed. Photochemical bromination was found to be inhibited by water and oxygen. The formation of alkenes by the dehydrobromination of the alkyl bromides was observed by temperature-programmed reaction to occur at higher temperatures for *n*-dodecane (~190 °C) than for the mixed alkanes in paraffin wax (~175 °C).



1. INTRODUCTION

Branched and linear saturated alkanes are among the most widely available commodity chemicals globally and a major constituent of petroleum. Their stability in nature is due in part to the strength of the carbon−hydrogen bonds, having a bond dissociation energy of approximately 410 kJ/mol.[1−4] Hence, the activation of the C−H bond is an essential step for functionalizing and transforming these building block molecules.[5] C−H bond activation in the chemical processing of alkanes often involves the use of high temperature oxidative conversions (>500 °C), leading to high capital costs and low selectivity for specific products.[6] The development of lower temperature (<250 °C), higher selectivity C−H bond activation and conversion chemistries might be beneficial for more efficient production of important chemical products.[7]

Higher olefins are an attractive class of chemicals, used in the production of a wide range of commodity products such as oligomers and polymers used in plastics, resins, fibers, elastomers, lubricants, surfactants, etc. However, the current processes for higher olefin production are either through the vapor-phase thermocracking of naphtha or the oligomerization of ethylene. Steam cracking is a highly energy intensive process and is associated with a significant amount of CO_2 production. Alternatively, lower energy processes for the production of higher olefins are therefore of value.

Low temperature C−H bond activation has been accomplished using a number of different mediators, including superacids,[8] organometallic catalysts,[9] and halogens.[10−12] Unlike oxygen, the use of halogens as oxidants offers a unique means of performing partial oxidation of the carbon in alkanes to produce important chemical intermediates without producing carbon dioxide as a byproduct. Among halogens, bromine is an attractive oxidant in terms of both reactivity and handling.

The organobromine compounds produced are versatile intermediates and precursors to carbocations, carbanions, carbon radicals and organometallic species.[13−16] Bromination can take place either in the vapor phase or in the liquid phase.[11] However, the bromination rate in the liquid phase is usually slower than in the vapor phase.[17] As a consequence, catalysts such as metallic chlorides and iodine are commonly employed for accelerating the rate of reaction. The use of catalysts requires that their lifetime, efficiency, and recycling do not impose unacceptable costs. The use of photoirradiation to initiate reactions that proceed through chain reactions can eliminate the need for a specific catalyst.[17]

The generally established mechanism for the bromination of alkanes using molecular bromine via a free radical reaction process is outlined in Scheme 1,[18] which also includes the final dehydrohalogenation reaction.

Bromine radicals are produced by the homolysis of molecular bromine (the initiation step). The homolytic cleavage of molecular bromine to form bromine radicals can be facilitated by heat or radiation. The free radical then abstracts a hydrogen atom from a C−H bond to form a carbon radical, liberating HBr gas in the process. Chain propagation is progressed by the

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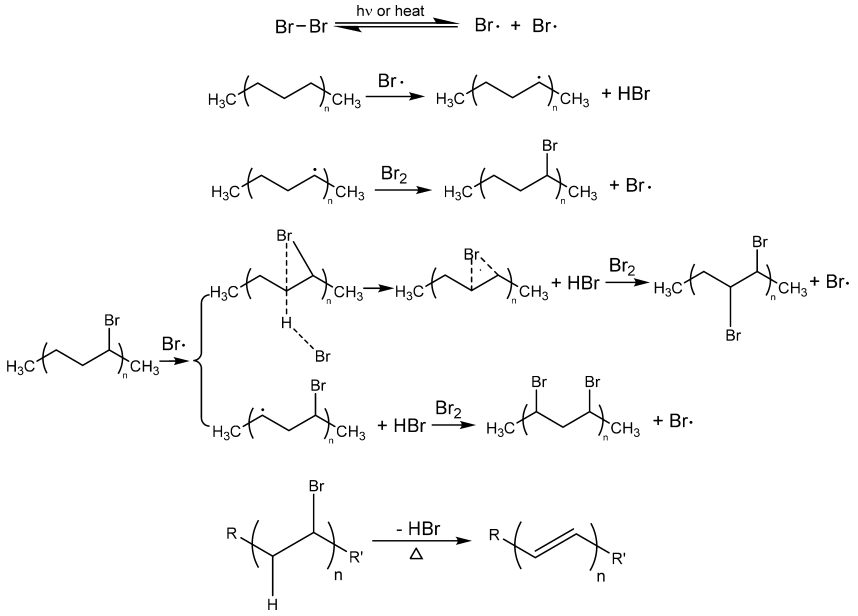
Scheme 1. Reaction Scheme for Free Radical Bromination and Subsequent Dehydrobromination



resulting carbon radical in turn abstracting a bromine atom from molecular bromine forming a C−Br moiety and regenerating another bromine radical. The eventual combination of two radicals (alkane and/or bromine radicals) terminates the reaction.

The fundamental processes involved in bromine substitution onto short chain alkanes (C_1−C_7) have been studied for decades. Egloff et al. summarized the outcomes in a very early review paper.[10] It was found that the four bromine derivatives of methane could be selectively obtained by varying the proportion of bromine to methane in the gas phase reaction under atmospheric or elevated pressure at 300−450 °C. Herzfelder[19] concluded that the main differences for the bromination reaction, as compared to chlorination, were that, unlike the relative ease of polychlorination (since the chlorine radical is much more reactive than the bromine radical), bromination proceeds only until each carbon atom has a single bromine atom attached. Further bromination can only happen under the most vigorous conditions, with a high risk of carbon chain rupture.

The preferential bromine substitution position follows the relative stability of the different free radicals, which is in the order of tertiary carbon > secondary carbon > primary carbon,[20] with tertiary C−H bonds having bond strengths of 93 kcal/mol, which are lower than secondary (96 kcal/mol) and primary (100 kcal/mol) C−H bonds. By the Hammond postulate, hydrogen abstraction by the bromine radical is an endothermic reaction with a late transition state, and with radical characteristics on the carbon involved in this transition state. Bromine is therefore much more selective for the tertiary carbon, such that the degree of substitution of tertiary carbons far exceeds the theoretical proportions, making this process a synthetically useful one for the preparation of tertiary alkyl bromides. Likewise, Anson et al.[21] found that bromine reacted more readily with isobutane than with the normal butane and, in a similar fashion, β-substitution is the primary product from the reaction of bromine with paraffins, while the bromination of the primary carbon was not observed.[10,22] As an example of innovation in this space, Paunović et al. recently reported the one-step gas-phase bromination of methane followed by catalytic HBr oxidation to recover active bromine.[23]

The type of radiation and heat source has also been found to affect the bromination rate and products. Bodroux and Taboury[24] found that the bromination of cyclohexane at boiling temperature was accelerated by both sunlight and ultraviolet light. Wood et al.[25] in turn observed that the reaction rate of cyclohexane bromination was proportional to the intensity of light absorbed. Blair et al.[26] observed the effect of water on the bromination reaction when passing *n*-hexane vapor into bromine in a stream of nitrogen. Interestingly, *p*-dibromobenzene and *trans*-benzene hexabromide were formed, although the reaction mechanism was not clear. Hormats and Van Artsdalen[14] found that the photobromination of neopentane in the temperature range of 98−152 °C, under constant irradiation by light of wavelength 405- 578 nm, was slowed down by small quantities of water and oxygen. Kharasch et al.[27] studied the individual effects of light and O_2 on the bromination of cyclohexane, methylcyclohexane, and isobutane. In this case it was found that the presence of oxygen promoted the bromination of cyclohexane and methylcyclohexane in the dark, while in the presence of light, bromination was accelerated in the absence of oxygen. The combined effects of O_2 and light on the bromination of cyclohexane, methylcyclohexane and isobutane were much greater than the sum of the individual effects. The authors tentatively proposed a reaction mechanism whereby oxygen is participating in the free radical chain reaction by competing with bromine radicals for the hydrocarbon radicals or by formation of unstable bromoxides (BrO_2, Br_2O). They also studied the photochemical vapor phase bromination of di- and tetra-methyl pentane (at low bromine concentrations) and proposed a hypothesis that olefins could be formed during the bromination process by disproportionation of a hydrocarbon radical, and the thus formed olefin then further reacted to produce di- and polybromides by addition of bromine.[27,28]

Except for a few short chain alkanes, the published work on bromination of longer chain alkanes (>C_8) is incomplete. In early studies,[10] researchers reported that little or no reaction

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was observed on bromination of alkanes with a chain length above C_{10} under low temperature conditions (<80 °C). Others observed bromoalkane production under more aggressive conditions, although the reactivity is much lower in the cases of long chain alkanes compared to the short chain alkanes. In 1964, for example, the Shell Research Laboratories[29] brominated *n*-decane by placing 1 mol in a distillation flask and heating to boiling under reduced pressure (115 mmHg) with UV irradiation placed along the Vigreux column. Bromine vapor was carried into the Vigreux column by N_2 gas at ca. 250 mmol/h. The reaction was stopped after 0.75 mol Br_2 had been introduced. The product mixture obtained comprised 66% decyl monobromide, 32% unreacted *n*-decane, and a small amount of dibromides. Ijam et al.[30] studied the temperature (40−120 °C) and irradiation effects on the bromination of a kerosene fraction (boiling point range 170−220 °C) and found that the reaction was most efficient at 85 °C in the presence of UV light of 350 nm. They also studied the bromination of decane, undecane, and dodecane with molecular bromine and showed that the product was mixtures of monobromides with traces of dibromides.[31] Gas and liquid phase bromination gave similar product distributions, and bromination at the primary carbons was not observed. In addition, the bromoalkanes produced were decomposed in the following separation process, i.e. distillation, into HBr and unsaturated hydrocarbons, which could then undergo further side reactions,[31] making the product identification complicated.[10] HBr is a volatile gas which can be readily captured and converted back into bromine through an energy-efficient, heterogeneously catalyzed, gas-phase oxidation.

We are interested in the bromination and dehydrobromination of long chain hydrocarbons. In this communication, results are presented for the photobromination and thermal dehydrobromination of pure dodecane and the mixed linear alkanes in paraffin wax. The reaction process is explored under an array of different conditions including differing temperatures, the presence of additives (water and oxygen), bromine:alkane mole ratios, and initiator sources (UV and thermal). The work presented addresses the following questions: (i) What conditions are suitable for bromine to be used to produce alkenes from long chain alkanes? (ii) How can the conditions be modified for photochemical bromine activation compared to thermal activation? (iii) Given that water and oxygen are the most common potential contaminants in these systems, what are the effects of such contaminants on the process?

2. EXPERIMENTAL SECTION

2.1. Materials. Paraffin wax (block form, white), dodecane (≥99%), and bromine (≥99.99%) were purchased from Sigma-Aldrich. Sodium thiosulfate pentahydrate (≥99%) was purchased from Chem-Supply Ltd. Oxygen was of a purity of 99.9%, and Milli-Q water was used throughout.

2.2. Methods. *2.2.1. Bromination of Alkanes.* The bromination of alkanes was completed inside slim quartz tubes with an inner diameter (ID) of 3 mm (wall thickness 1.5 mm) and initial length of 170 mm. In a typical experiment, the alkane and bromine were loaded into the tube and temporarily sealed using a Teflon lined rubber septum, then cooled in dry ice while being evacuated on a Schlenk line equipped with a diffusion pump to a pressure of 5×10^{-2} atm or lower. In the specific instances where additives were required, H_2O was added to the tubes in the initial loading along with the alkane and bromine during evacuation, while O_2 was injected into the tubes using a gastight syringe following evacuation.

Samples were then flame-sealed to approximately 3/4 of their original length with liquid sample frozen at the bottom of the tube by immersing in liquid nitrogen. The sealed quartz tubes were then placed inside an SEM gravity convection oven with internal dimensions of 20 cm × 25 cm × 20 cm ($h \times w \times d$) at the prescribed temperature with or without a light source applied. The light source was a 15 W, 415 nm LED UV light bulb purchased from Bridelux, Shenzhen, China. The distance between the samples and light source was 7 cm. After bromination, tubes were cooled first in dry ice, then opened with the aid of glass cutters and the products quenched using sodium thiosulfate pentahydrate (0.5−2 g depending on the amount of bromine residue) before dissolving in $CDCl_3$ (~0.6 mL) to remove any residual bromine. Each experiment was run twice. The standard deviations were calculated from the resulting data and added as error bars in all figures.

2.2.2. Physiochemical Characterization. Given the high volatility of bromine, titrimetric approaches for quantifying the residual (unreacted) bromine were not found to be sufficiently accurate. Samples from the bromination of dodecane and paraffin under a broad range of reaction conditions were analyzed by NMR. NMR spectroscopy of the products of bromination of dodecane and paraffin under a broad range of reaction conditions was used as the primary method for product analysis. This is because any methods that rely on a thermal stage, such as gas chromatography, are confounded by the effect of dehydrobromination of these materials at temperatures as low as 140 °C, with the possibility of further reaction and cross-linking at these temperatures. High-resolution NMR spectroscopy was carried out on a BRUKER 700 Avance III HD with a 3-channel 5 mm TCI cryoprobe at a constant temperature of 298 K. All data were acquired with TOPSPIN v3.2 and processed using MestReNova v9.1. The ^{1}H, ^{1}H-COSY, DEPT-135, and ^{1}H,^{13}C-HSQC experiments enabled approximate peak assignments for classes of reaction products. The NMR samples contained approximately 20 μg liquid sample dissolved in 600 μL $CDCl_3$ and spectra were referenced to the solvent signal at 7.260 ppm. ^{1}H spectra were recorded with a zg30 pulse sequence, 16 scans, a relaxation delay of 0.1 s, and a pulse width of 8.07 ms. ^{13}C spectra were recorded with a zgpg60 pulse, 452 scans, a relaxation delay of 0.84 s, and a pulse width of 11.9 ms. DEPT spectra were obtained using the deptsp135 pulse sequence with 1024 number of scans, a relaxation delay of 1.4 s, a pulse width of 11.9 ms, and a sweep width of 111 ppm. ^{1}H,^{1}H-COSY experiments were performed with a cosygpqf pulse sequence, 2 scans, a relaxation delay of 2 s, and a spectral width of 8.5 ppm. ^{1}H,^{13}C-HSQC were performed with a hsqcetgpsisp2.2 pulse sequence, 8 scans each, a relaxation delay of 1 s, a pulse width of 8.07 ms, and sweep widths of 8.5 and 111 ppm for the ^{1}H and ^{13}C dimensions, respectively.

The percent substitution of the CH protons on the alkanes by bromine were calculated from ^{1}H NMR spectra according to the following procedure: Assume that the integral for CHBr = x (based on the integral for the region between 3.95 and 6.50 ppm, region E and F in Figure 1), for CH_2 = y (based on the integral for the region between 1.15 and 1.69 ppm and 1.73 and 3.95 ppm, region B and D in Figure 1), and for CH_3 = z (based on the integral for the region between 0.75 and 1.15 ppm and 1.69 and 1.73 ppm, region A and C in Figure 1). Then, also assuming that there is no Br−C−Br formed, which is justified

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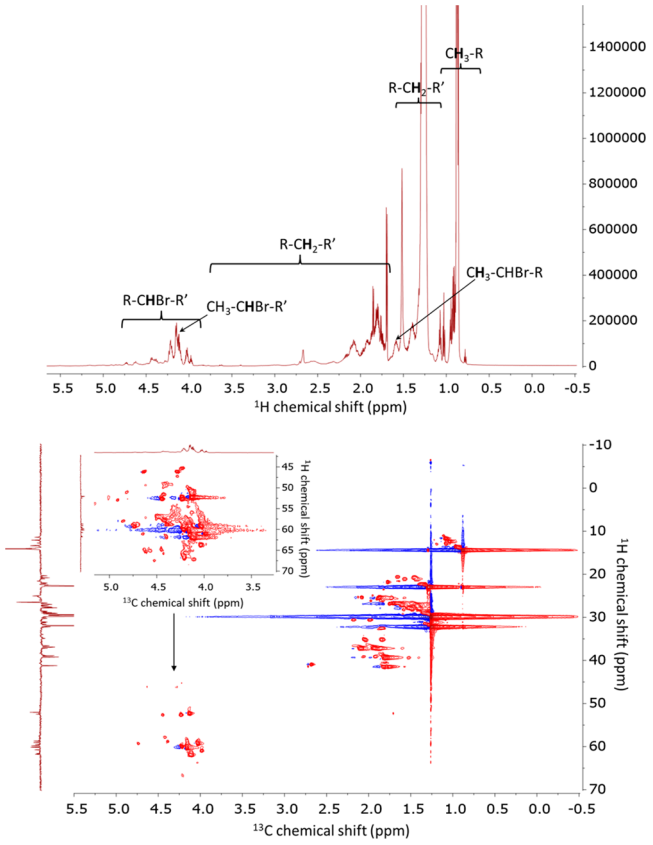

Figure 1. Example of ^{1}H NMR spectrum (top) and ^{1}H,^{13}C-HSQC spectrum (with DEPT-135 spectrum on the *Y*-axis) (bottom) of brominated dodecane (reacted using a mole ratio Br_2:CH_2 = 1:1 for 1 h at 90 °C under vacuum 1.5 mbar).

based on the ^{13}C NMR spectra, and that the formation of C═C bonds can be ignored at this point, which is also justified based on both the ^{1}H and ^{13}C NMR spectra, then assume that the CHBr peaks evolved from CH_2 or CH_3 through substitution of one hydrogen. Thus, by doubling the integral for x and adding it to $y + z$, represent the relative integral for the starting material, which therefore can be given by eq 1.

$$\text{percent substitution of CH by CBr} = \frac{x}{2x + y + z} \times 100\% \quad (1)$$

Gas chromatography-mass spectrometry (GC-MS) was performed on a SHIMADZU, GCMS-QP2010 Ultra gas chromatograph mass spectrometer, equipped with a 30 m Rtx-5MS column (thickness 0.10 μm, diameter 0.25 mm). The GC oven temperature was kept at 50 °C for 3 min, then heated at a rate of 20 °C/min until the oven temperature reached 230 °C. After holding at 230 °C for 10 min, the oven was then cooled.

The temperature at which dehydrobromination of the alkyl bromides occurs to form an alkene and hydrogen bromine was observed by analysis of the evolution of HBr from brominated dodecane or paraffin wax using temperature-programmed reaction spectroscopy (TPR). In order to observe the reaction products as a function of temperature after bromination occurred, samples of brominated paraffin wax and brominated dodecane were heated in 16 sccm flowing Ar passing over the surface of the brominated alkanes whose effluent was connected to a SRS RGA 300 mass spectrometer using a Hastelloy union tee with graphite ferrules. After brominating according to the procedure described in section 2.2.1, the samples were first opened by breaking the glass top, and then the bottom of the tube containing the liquid or solid sample was immediately placed on a quartz wool bed inside a 1/2 in. ID quartz tube with 10 sccm Ar flowing over the tube. The entire assembly was place in a custom heater block with a uniform temperature profile over the sample area and ramped at 2 °C/min from 30 to 200 °C before being held at 200 °C for 180 min. All tubing downstream was constructed from glass and heated to 130 °C to prevent HBr or H_2O from condensing or reacting with the tubing. A glass capillary tube was teed in directly to the HBr calibrations which were performed using high purity HBr gas. The partial pressure of HBr was determined using peak 82 in the mass spectrometer and an appropriate sensitivity factor applied from calibrations.

3. RESULTS AND DISCUSSION

3.1. Bromination of Long Chain Alkanes. Representative spectra from the products of bromination of dodecane and paraffin are shown in Figure 1. From the DEPT spectra, which allows assignment of CH_2 versus CH_3 and CH resonances in the carbon spectra, it was evident that there were no resonances, even at high degrees of substitution, which could be assigned to CBr_2, since there were no resonances in the region below 100 ppm which remained unaccounted for, i.e., they were all assigned as CH, CH_2, or CH_3. There was also no evidence that alkenes were forming at temperatures below 120 °C.

Figure 2 provides a summary of the integrated ^{1}H NMR spectral data accumulated across all experimental conditions for

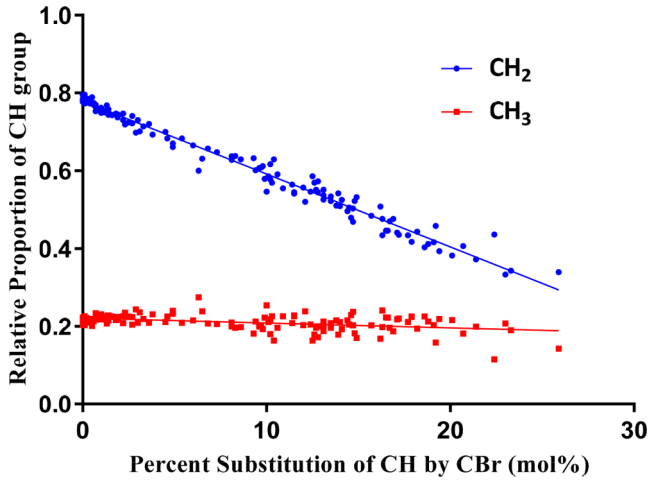

Figure 2. Relative peak areas in the ^{1}H NMR spectra for the CH_3 and CH_2 regions of the spectra; calculations of relative proportions are based on eq 1, setting $2x + y + z$ to 1.

the bromination of dodecane (as described below). The data shows little change in the CH_3 resonance integrals with increasing bromination compared to the strong dependence of the CH_2 resonance integral on increasing bromination. What little decrease is observed in the CH_3 integrals may be due to peak shifts into the nominal CH_2 region. This data supports the preferential abstraction and substitution of methylene group protons by bromine compared to reaction at the methyl group.

Combinations of photo- and thermally induced bromination of paraffin wax and dodecane are summarized in Figure 3.

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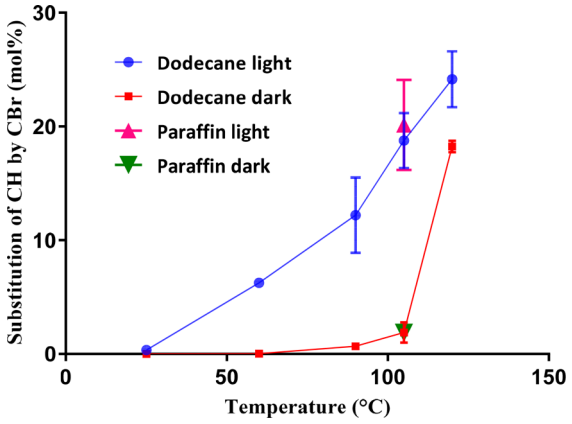

Figure 3. Ultraviolet versus thermally initiated bromination of dodecane and paraffin wax as a function of temperature (mole ratio Br_2:CH_2 = 1:1, reacted for 2 h under vacuum).

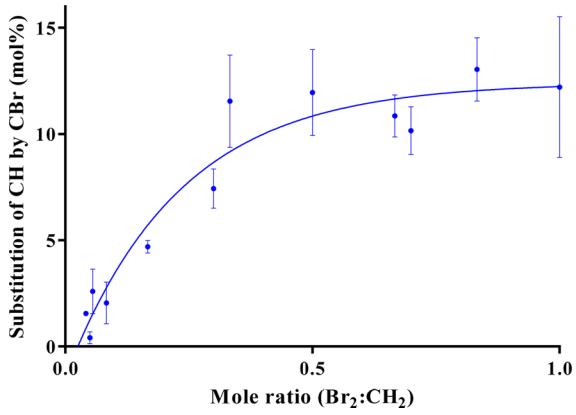

Figure 4. Effect of mole ratio of Br_2:CH_2 on photobromination yield for dodecane (reacted at 90 °C, 2 h, vacuum atmosphere, under UV irradiation).

Under constant illumination of ultraviolet light, a steady qualitatively monotonic increase in percent bromination was observed between room temperature and 120 °C. Given that no substitution takes place at the methyl group and that each secondary carbon is only substituted by a single bromine atom (based on spectroscopic analysis as well as GC/MS analysis of the reaction products), then the theoretical maximum percent substitution of CH_2 to CHBr is 38% (= 10/26) for dodecane and 45% (= 29/64) for paraffin wax ($C_{31}H_{64}$). On that basis, approximately two-thirds of the available methylene groups were singly substituted after 2 h at 120 °C under UV irradiation.

The temperature dependence of the radical mediated dodecane bromination without light, observed in Figure 3, is consistent with an initiation limited thermal reaction below approximately 105 °C, whereby the thermal activation of bromine is rate limiting and controls the overall reaction rate. With light mediated bromine activation, initiation to produce bromine radicals is no longer rate determining and the near linear temperature dependence of the rate is consistent with a negligible effective activation energy for the other reaction pathway steps. This behavior is consistent with that observed by Ramage and Eckert in the chlorination of dodecane.[32]

At temperatures above 105 °C, the degree of substitution increased significantly such that approximately 50% of the methylene groups were substituted after 2 h at 120 °C in the dark. Samples of paraffin wax exhibited very similar results to those of dodecane. At temperatures above 105 °C light is not needed, whereas photoinitiated bromine activation allows for significant reaction rates at lower temperatures.

As shown in Figure 4, the effect of the relative molar ratio of bromine to methylene groups was also explored at 90 °C under UV irradiation. At low bromine loadings, substitution of C−H by C−Br increased approximately linearly with increasing bromine up to ∼0.4 mol Br_2 to moles CH_2. At higher bromine to CH_2 ratios, there was limited additional substitution with an apparent saturation at ∼10% substitution of C−H by C−Br. This represents approximately one-quarter of the available methylene groups substituted.

Nearly complete bromine substitution for the available methylene protons would be expected in excess bromine together with polybromination. The limited bromination observed might be due to significant UV light absorption by the excess Br_2 in the sample tube limiting the penetration of light into the bulk material and thus restricting the overall extent of reaction. The effect of light penetration on an industrial scale process will therefore need further detailed study, including an analysis of mean diffusion pathways, for full implementation of such a strategy. In addition, there may be diffusion effects such that if the surface layers are more heavily brominated than the hydrocarbon bulk, the brominated surface hydrocarbons might require time to diffuse away and likewise allow the less reacted bulk to diffuse into a region where molecules are more exposed to the light. Alternatively, the reaction time may be limiting the extent of bromination.

In Figure 5 the reaction time was increased and dodecane bromination at two different temperatures and two different mole ratios of Br_2:CH_2 was determined. The 1:1 mol ratio samples reached the same extent of bromination (∼27% overall, i.e. around 70% of the methylenes reacted), which was achieved in only 2 h at 120 °C while it took 8 h at 90 °C to reach the same degree of substitution. The rate of increase in fractional substitution was approximately constant, indicating that it was less likely that it was slowed by a steric effect (the effects of which should increase as the degree of substitution increases).

At a lower bromine loading (10:1 CH_2:Br_2), there may have been a small increase in the rate of substitution at the higher temperature (120 °C c.f. 90 °C). However, after 10 min, the percent C−H substitution by C−Br at these low bromine additions was constant at ∼2−3%. If all the bromine reacted, around 10% of the methylene groups should be substituted. The slightly inconsistent results could be attributable to experimental error when such small volumes of Br_2 are being added.

Overall, it is possible to achieve a high degree of substitution of the methylene groups in higher alkanes under relatively mild conditions using either temperature alone above 105 °C, with prolonged reaction, or through acceleration of the reaction using ultraviolet irradiation combined with increasing temperature.

3.2. Effect of O_2 and H_2O on the Photobromination of Dodecane. Data from a series of bromination experiments conducted at different temperatures with the addition of small amounts of water and/or oxygen are summarized in Table 1. Overall, there was inconsistency with respect to the effect of addition of water and/or oxygen on the rate of bromination. At the lower temperature (90 °C), there was a statistically

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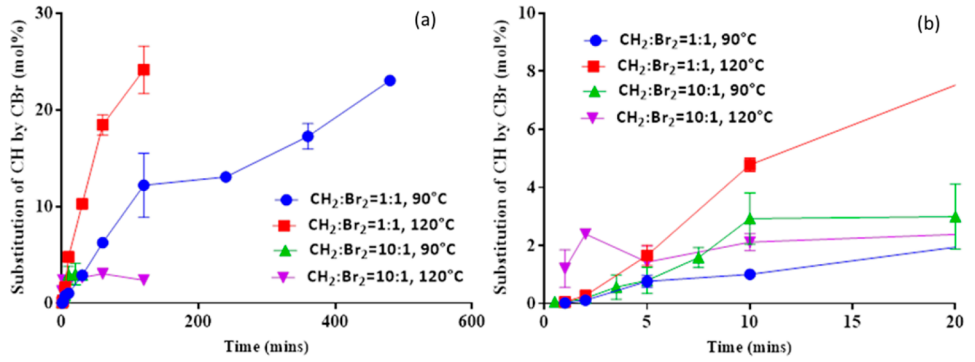

Figure 5. Photobromination of dodecane at different temperatures and mole ratios of Br_2:CH_2 for increasing reaction times: (a) full scale; (b) enlarged.

Table 1. Effect of Water and/or Oxygen on the Photobromination of Dodecane[a]

temperature (°C)	O_2 (mL)	H_2O (μL)	percent substitution of CH by Br
90	0	0	15.4 ± 2.5
90	1	0	11.5 ± 0.1
90	0	50	8.9 ± 1.1
90	1	50	6.4 ± 1.4
105	0	0	18.8 ± 2.4
105	0.2	0	16.3 ± 2.2
105	0.5	0	16.7 ± 3.9
105	1	0	13.5 ± 7.7
105	0	5	13.3 ± 5.2
105	0	10	15.1 ± 2.2
105	0	50	20.0 ± 4.8
105	0.2	5	15.8 ± 4.6
105	0.2	10	12.5 ± 0.5
105	0.2	50	13.6 ± 3.0
105	0.5	5	16.9 ± 5.3
105	0.5	10	13.7 ± 1.7
105	0.5	50	13.7 ± 0.4
105	1	5	15.7 ± 1.2
105	1	10	12.4 ± 3.0
105	1	50	12.6 ± 1.7

[a]Mole ratio Br_2:CH_2 = 1:1, 2 h, UV irradiation.

significant reduction ($p < 0.05$) in the percent substitution of C−H by C−Br on addition of these environmental contaminants. The NMR spectra did not show evidence of carbonyls or other obvious oxidation products and thus the most likely explanation is the trapping and quenching of free radicals by water and/or oxygen. By contrast, there was much more variability in the data from trials run at the higher temperature (120 °C), making it more difficult to draw a conclusion apart from noting with caution that there were instances where a significant decrease in bromination yield was observed.

3.3. Dehydrobromination of Brominated Dodecane and Paraffin. The HBr detected by mass spectrometry from dehydrobromination of brominated paraffin and brominated dodecane during TPR is shown in Figure 6. The alkyl bromides had been prepared in a separate reactor at 120 °C under a 2 h illumination with UV using a 1:1 Br_2:CH_2 mole ratio. Dehydrobromination of both brominated paraffin and brominated dodecane displayed similar temperature profiles, with the onset temperature for dehydrobromination being slightly higher for dodecane (~190 °C) than for paraffin wax (~175 °C), which may be related to the fact that paraffin wax has branching and thus weaker tertiary C−Br bonds. The irregularities in the dodecane curve are consistent with the boiling of unreacted dodecane liquid when the temperature approached its normal boiling point.

Mass balance was determined using the integral of the calibrated HBr signal. Based on the weight of the brominated dodecane before dehydrobromination, there are 0.45 HBr molecules evolved per carbon atom. The NMR-based results for dodecane brominated under the same conditions suggest

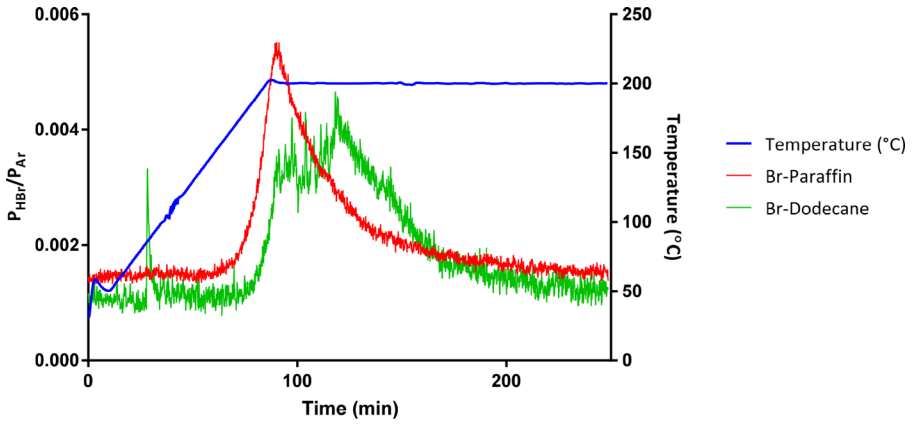

Figure 6. TPR data for the HBr evolution measured by mass spectroscopy during the heating of brominated dodecane and brominated paraffin wax: (red) brominated dodecane, (blue) brominated paraffin wax.

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that ~27% of the carbons were coordinated to bromine after bromination. HBr is known to have a limited solubility in paraffins and other alkanes (at 0.06 mol HBr per mole decane at 293 K, for example, with solubility decreasing with temperature) and as such it is readily recovered in a volatile (gaseous) form following release through off-gassing.[33] Therefore, the result may due to HBr being soluble in brominated dodecane but not in dodecene or related products (formed after dehydrobromination). We conclude that the HBr liberated from H abstraction of the C−H bond may have accumulated in the dodecane/brominated dodecane mix during bromination under a pressured environment and remained within the hydrocarbon mixture during purging and heating to ~190 °C.

As previously noted (section 3.1), the initial bromination occurred at the secondary carbons, with subsequent bromination on the paraffin chain being affected by the location of the initial C−Br bond through free radical stabilization.[34−36] Since in this case we are maximizing the degree of bromination, the double bonds formed after dehydrobromination are thus present in a complex mixture and hence we were unable to characterize with any certainty the location of such bonds through NMR analysis.

4. SUMMARY

The bromination of higher alkanes is a facile pathway for the activation of C−H bonds. The use of ultraviolet photochemical initiation enabled lower temperature bromination (~90 °C) albeit at rates four times slower than at 120 °C. Thermal bromination occurred at increasingly significant rates above 105 °C. A nonlinear response to an increase in bromine loading was observed. UV initiated photobromination was inhibited by water and oxygen, which are common environmental contaminants expected in most applications. Dehydrobromination to form the desirable higher alkenes occurs readily at temperatures between approximately 175 and 190 °C.

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Notes

The authors declare no competing financial interest.

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