Water-in-Oil Emulsion Foaming by Thiourea Nitrosation: Reaction and Mass Transfer

Gabriel da Silva, Bogdan Z. Dlugogorski, and Eric M. Kennedy
Process Safety and Environment Protection Research Group, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

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A study has been undertaken into the chemical production of gas bubbles within a concentrated water-in-oil emulsion, typical of those used as emulsion explosives. Chemical foaming was initiated by the introduction of a concentrated sodium nitrite solution to the emulsion, and the measurement of the decreasing emulsion density with time served to estimate the rate of nitrogen production. A conversion of emulsion density to nitrite ion concentration facilitated a kinetic analysis of the data. The change in nitrite ion concentration follows a rate equation which indicates that the rate-limiting reaction step corresponds to the N-*nitrosation of thiourea by* ON^+*, with an apparent rate constant of* $0.22\ M^{-1}\ s^{-1}$ *at 25 °C. Tests over a temperature range of 25 to 50 °C yielded an activation energy of* $59\ kJ\ mol^{-1}$*. A mass-transfer model describing the rate of diffusion between aqueous droplets is presented. This model suggests that chemical kinetics, rather than molecular diffusion, is the rate-limiting phenomenon in the foaming of emulsions. Supporting this finding, the kinetic experiments in emulsion returned very similar results to previous experiments performed in aqueous media under similar conditions.* © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1558-1565, 2006

Introduction

Foamed emulsions constitute complex three-phase fluids, typically consisting of large gas bubbles stabilized within either an oil-in-water or water-in-oil emulsion. Common applications of foamed oil-in-water emulsions include food processing,[1-3] antifoaming,[4,5] pharmaceuticals[6] and enhanced oil recovery.[7] Also, foams of this type have received considerable attention in the literature due to the ability of the oil phase to affect the stability of the air/water interface by way of pseudoemulsion film formation.[8-12] However, foamed water-in-oil emulsions find fewer applications.

Emulsion explosives, used extensively within the mining industry, comprise a significant class of foamed water-in-oil emulsions. Emulsion explosives consist of an aqueous phase (oxidizer), dispersed within a continuous oil phase (fuel). Generally, the aqueous phase corresponds to a supersaturated solution of ammonium nitrate, and/or other nitrate salts, while a hydrocarbon based fuel such as fuel oil or paraffin wax forms the continuous phase.

In order for an emulsion explosive to detonate, it must first be sensitized. Sensitization involves introducing small low-density voids into the emulsion matrix, which provide hot spots at which the explosion may nucleate.[13-16] Sensitization necessitates distributing material of a hollow or porous nature throughout the emulsion, or by generating gas bubbles *in situ*, via chemical reaction.[17,18] The use of chemical reaction to produce voids within emulsion explosives is often referred to as chemical gassing, and this process has emerged as one of the most efficient and cost-effective means of explosive sensitization.[19]

Chemical gassing of an emulsion explosive proceeds via the addition of a concentrated nitrite salt solution to an emulsion, where it reacts with ammonia (present due to ammonium nitrate), yielding nitrogen gas via a nitrosation mechanism.[20,21] Gas bubbles produced by chemical gassing range from around

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Correspondence concerning this article should be addressed to B. Z. Dlugogorski at bogdan.dlugogorski@newcastle.edu.au.

80 to 400 μm in size,[17,22] compared to dispersed phase droplets of about 10 μm. These gas bubbles are stabilized by surface active molecules present in the oil phase of the emulsion.[17] Typical gas voidage in emulsions of this type is around 30% by volume.

The major disadvantage of chemical gassing is that it is very slow, and long mine-site delays are often encountered before an explosive is ready to detonate. As such, certain reagents are added to accelerate the gassing process. One means of catalysing nitrosation reactions is by the addition of strong nucleophilic species, such as thiocyanate, which accelerate the gassing reaction through increased equilibrium concentration of the effective nitrosating agent.[23]

A successful approach to accelerating the rate of chemical gassing is to replace ammonia with a more reactive substrate. Thiourea ($CS(NH_2)_2$) is a commonly used substrate,[24] which is particularly effective at increasing the rate of reaction. Thiourea undergoes nitrosation at both sulfur and nitrogen sites, and it has recently been shown that *N*-nitrosation of thiourea is the dominant nitrosation mechanism at concentrations used in chemical gassing.[25] The *N*-nitrosation of thiourea follows the overall stoichiometry of Eq 1. In this mechanism, the species ON^+ (from HNO_2) acts as the effective nitrosating agent.[25,26]

$$HNO_2 + SC(NH_2)_2 \rightarrow N_{2(g)} + 2H_2O + HSCN \qquad (1)$$

Chemical gassing using thiourea still proceeds relatively slowly at ambient temperatures. This is particularly an issue at either cold or remote mine sites, where the emulsion may cool dramatically from its production temperature of about 70 °C. The intrinsic chemical kinetics of the nitrosation reactions that occur within emulsion explosives are well studied for idealized aqueous systems.[24,25] However, the effect of conducting these reactions within an emulsion remains poorly understood.

Two possible rate-controlling regimes need to be considered when studying nitrosation kinetics within emulsions and microemulsions:[27,28] chemical kinetics and molecular diffusion. When a sodium nitrite solution is added to an emulsion explosive, discrete emulsion droplets of a third phase are formed. Diffusion must occur between the droplets of sodium nitrite and the droplets of supersaturated ammonium nitrate, across thin oil films, before chemical reaction can take place. If this diffusion process is slow, it may limit the overall process of nitrogen gas production. However, if mass transfer is rapid, then the system behaves as if the nitrite ions are homogeneously dispersed within the aqueous phase of ammonium nitrate, with the process being controlled by chemical kinetics.

In addition to the multiphase macrodiffusion discussed earlier, a further form of mass transfer limitation may be present during chemical gassing. This phenomenon is known as encounter-controlled diffusion, and results from the rate of chemical reaction being greater than the rate at which the reacting species can diffuse from within their respective solvent cages to form an encounter pair. Encounter-controlled diffusion occurs when particularly reactive combinations of nitrosating agent and substrate undergo reaction, and this phenomena is well studied for nitrosation reactions.[29-31] Under conditions of encounter-control, second-order rate constants are typically limited to values of no greater than 10^{10} M^{-1} s^{-1} as predicted by mass transfer theory. Also, encounter-controlled activation energies are typically of the order of 20 kJ mol^{-1} or less, as compared to typical values of 50 – 90 kJ mol^{-1} for reaction-controlled conditions. The magnitude of an observed activation energy may be misleading, as an activation energy of around 20 kJ mol^{-1} would be expected for systems under either macrodiffusion-control or encounter-control, therefore complicating the identification of these two dissimilar forms of diffusion.

A number of studies have been published concerning the properties of foamed emulsion explosives, as a consequence of their industrial significance. The factors affecting the emulsion morphology,[21,32-34] rheology,[35] stability[17,36] and detonation[37-40] are all reasonably well understood. However, little is known about the kinetics and mechanism of chemical foaming, especially about the role played by mass-transfer resistance. This is even though the chemical gassing process often limits mine productivity due to the slow kinetics. In addition, nitrosation reactions conducted in heterogeneous media find other applications,[27,28] for which the role of mass transfer limitation has not been studied. As such, we have undertaken an investigation into the mechanism of the chemical foaming of an emulsion explosive consisting of a supersaturated solution of ammonium nitrate (with thiourea added as an accelerant), dispersed in fuel oil. This study particularly focuses on whether or not the chemical gassing process is controlled by mass transfer or chemical reaction. We begin by modeling the rate of chemical gassing under macro-diffusion-controlled conditions. Following this, experimental gassing results are examined to determine the rate controlling reaction step.

Materials and Methods

Emulsion composition

Aqueous Phase. The aqueous phase consisted of 80% ammonium nitrate and 20% water (by weight). This solution was heated to above 70 °C and stirred for several hours, so as to facilitate complete ammonium nitrate dissolution. Thiourea was added to the mixture at 1.5 g/kg, with sodium carbonate added as buffer at 0.43 g/kg. Once complete dissolution had occurred, the solution was adjusted to a pH of 3.9 using glacial acetic acid.

Oil Phase. The oil phase comprised a mixture of 73 wt % fuel oil and 27 wt % emulsifier. The emulsifier used is that employed previously by Turner et al.,[17] and contains the reaction products of poly[alk(en)yl]succinic anhydrides and alkylamines, including the polyisobutylene (PiBSA) derivatives of alkanolamines.

Emulsion Preparation. The emulsion was prepared at the ratio of 92% aqueous phase to 8% oil phase. Emulsification was conducted in 3 kg batches, in a heated mixing bowl. The oil phase was first placed in the bowl, mixed gently and heated to 50 °C. The hot aqueous phase was then slowly added, while mixing was maintained so as to ensure emulsification. Once the two phases were emulsified, rapid mixing was undertaken for a period of 10 min, so as to obtain a monomodal distribution with droplets of around 10 μm.[17] The emulsion was then left to cool to room temperature before gassing.

Gassing. Gassing experiments were carried out by mixing 2 g of a 33 wt % sodium nitrite solution per kg of emulsion. Mixing was conducted for 30 s using an impeller to blend approximately 400 g of emulsion with the required amount of

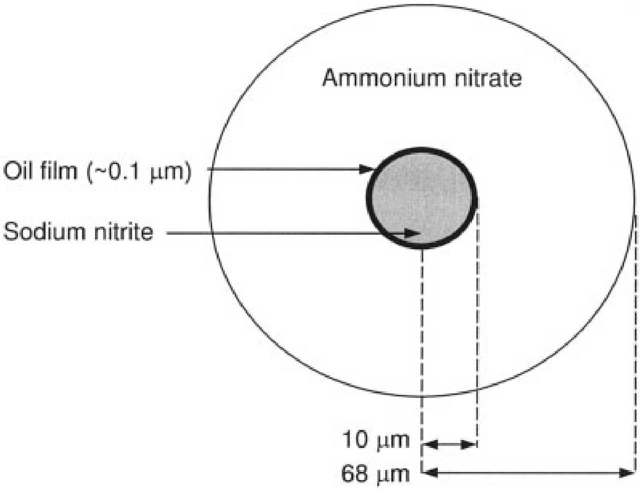

Figure 1. Mass-transfer model for the chemical gassing of an emulsion explosive.

sodium nitrite solution. Once mixing was complete, a disposable 209 cm^3 plastic cup of known weight was packed with emulsion, and leveled off to the rim. The full cup was weighed, and then placed in a temperature controlled oven. Periodically, the cup was removed from the oven for density measurements of the foamed emulsion. Density measurements consisted of removing any excess emulsion from the top of the cup, and recording the new weight. Density was calculated by dividing the weight of emulsion in the cup by the total cup volume.

Mass-Transfer Modeling

Model development

In this section we attempt to establish, by means of an approximate analysis, that mass-transfer processes during emulsion foaming take place at the rate of several orders of magnitude faster than chemical reaction. To this end, we first construct a simplified model of the system. This model assumes that upon mixing, the sodium nitrite solution forms discrete droplets of 10 μm radius. In order for mass-transfer effects to be neglected, the nitrite droplet and the surrounding droplets of ammonium nitrate must become completely homogeneous. For this to occur, the nitrite ions dissolved in each sodium nitrite droplet must undergo diffusion throughout the corresponding volume of the solution of aqueous ammonium nitrate (3.6×10^{-12} m^3 per sodium nitrite droplet). Similarly, between droplets of the aqueous phases, one finds 3.1×10^{-13} m^3 of fuel oil per droplet of sodium nitrite. An illustration of this simplified model is drawn in Figure 1 (not to scale), where all droplets of emulsion surrounding a single droplet of sodium nitrite are represented by a large spherical droplet of ammonium nitrate (of volume equivalent to that of both the oil and ammonium nitrate phases) centered on the sodium nitrite droplet. In the model, the two phases are separated by a single thin oil film, approximately 0.1 μm in thickness.

The mass-transfer steps between the sodium nitrite and ammonium nitrate droplets include the diffusion of acetic acid, ammonia and thiourea into the sodium nitrite droplets, and the diffusion of nitrite ions, nitrous acid and ON$^+$ back out of the sodium nitrite droplets. However, we are able to safely neglect many of these steps. First, due to the relatively small volume occupied by the sodium nitrite droplets, we may assume that the production of nitrogen gas occurs solely in the ammonium nitrate phase, with bubble growth occurring in the oil phase,[17] thus, allowing us to ignore any diffusion of the substrates (that is, ammonia and thiourea) into the droplets of sodium nitrite. The diffusion of nitrite ions (or ON$^+$) into the ammonium nitrate phase will be slow, due to the low solubility of nitrite ions within the surrounding oil phase. Therefore, diffusion of nitrous acid out of the sodium nitrite droplet will be rate limiting.

From the preceding analysis, the significant mass-transfer steps involve the diffusion of hydrogen ions into the sodium nitrite droplet, across a single thin oil film, and the subsequent diffusion of nitrous acid back into the emulsion. During the first step, hydrogen ions largely exist as undissociated acetic acid (CH_3COOH), due to the pH of the system and the pK_a of acetic acid (3.4) (as shown in Figure 2). In the aqueous ammonium nitrate solution, acetic acid exists at a concentration of around 0.063 M. For the complete conversion of all nitrite to nitrous acid, a total of 2.6×10^{-11} mol of acetic acid must diffuse into a single sodium nitrite droplet, reducing the bulk acetic acid concentration to 0.056 M. Following this step, nitrous acid diffuses out of the sodium nitrite droplet, from an initial concentration of 4 M, to a final homogeneous concentration of 0.028 M. Here, diffusion through both the oil and ammonium nitrate phases is significant (Figure 2). Also, as a further simplification, the model depicted in Figure 2 shows diffusion occurring through a flat film, as opposed to a spherical surface.

To model the two significant diffusion steps we must first obtain either experimental or estimated diffusion coefficients for acetic acid in water, and nitrous acid in both water and fuel oil. The diffusivity of acetic acid in water (at infinite dilution and 20 °C) has been determined as 1.2×10^{-9} m^2 s^{-1}.[41] For the remaining values, we have made estimates using the Wilke-Chang correlation (Eq. 2)

$$D^{\circ}_{AB} = \frac{7.4 \times 10^{-8}(\phi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \tag{2}$$

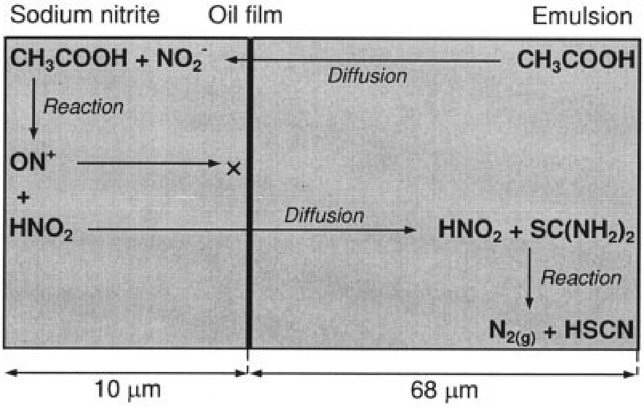

Figure 2. Significant mass transfer and reaction steps in the chemical gassing of an emulsion explosive.

The polar species ON$^+$ cannot diffuse across the oil film.

where D^{o}_{AB} is the diffusion coefficient of solute A, at infinite dilution, in solvent B ($cm^2\ s^{-1}$), M_B is the molecular weight of solvent B ($g\ mol^{-1}$), T is the temperature (K), μ_B is the viscosity of solvent B (cP), V_A is the molar volume of solute A at its normal boiling point ($cm^3\ mol^{-1}$), and ϕ is an association factor of the solvent B.

For nitrous acid, V_A has been estimated as 36 $cm^3\ mol^{-1}$ using the additive volumes of Le Bas.[42] The viscosity of water is 1 cP, while that of the oil phase is about 0.8 cP. The respective molecular weights of water and oil are 18 and 128 $g\ mol^{-1}$ (the oil phase has been modeled as naphthalene, a major component in most fuel oils). The association factor has been taken as 2.6 for water, and 1.0 for the oil phase. Using the above values, and a temperature of 298 K, we obtain diffusion coefficients of 9.5×10^{-8} and 2.0×10^{-9} $m^2\ s^{-1}$ for the diffusion of nitrous acid in water and in fuel oil, respectively.

For the diffusion of nitrous acid through the emulsion, the rate of diffusion will depend on both the diffusivity and solubility of nitrous acid in both oil and water. From the above, we note that the respective diffusion coefficients are similar in magnitude. Also, observing that nitrous acid is a nonionic molecule, it is soluble in both phases. As such, we may assume that the rate of diffusion of nitrous acid in both phases will be comparable, allowing us to make the simplification that diffusion out of the sodium nitrite droplets occurs through a single phase, having the properties of water, and the combined volume of the oil and ammonium nitrate phases. Also, by similar reasoning, we may neglect diffusion through the single oil film for diffusion of acetic acid into the sodium nitrite droplet. This particular assumption is strengthened by the fact that the thin oil film through which diffusion occurs is of thickness no greater than approximately 0.1 μm.

Diffusion across droplet boundaries may be modeled using Eq. 3 for diffusion across a thin film

$$N_{Az} = \frac{CD_{AB}}{z_2 - z_1} \ln\left(\frac{1 - x_{A2}}{1 - x_{A1}}\right) \tag{3}$$

where N_{Az} is the molar flux of A in the z direction ($kmol\ m^{-2}\ s^{-1}$), C is the total concentration ($kmol\ m^{-3}$), and x_{A1} and x_{A2} are the mole fractions of A at positions z_1 and z_2, respectively.

Diffusion of acetic acid

For diffusion into a sodium nitrite droplet according to Eq. 3, mass transfer occurs from the droplet boundary ($z_1 = 0$ μm) to the center of the droplet ($z_2 = 10$ μm) (see Figures 1 and 2). The acetic acid concentration at position z_1 initially equals 0.063 $kmol\ m^{-3}$, and drops to a final value of 0.056 $kmol\ m^{-3}$. The total molar density of the sodium nitrite droplet is 59 $kmol\ m^{-3}$, giving initial and final x_{A1} values of 1.1×10^{-3} and 9.5×10^{-4}, respectively. Under conditions of complete mass transfer control, which implies instantaneous chemical reaction, the concentration of acetic acid within the sodium nitrite droplet is zero at all times (that is, $x_{A2} = 0$).

As an approximation, the average molar flux over the course of the reaction, under diffusion-controlled conditions, may be calculated as the log mean average of N_A obtained for the initial and final acetic acid concentrations. This calculation has been performed, yielding an average molar flux of 5.9×10^{-6} $kmol\ m^{-2}\ s^{-1}$. As diffusion is occurring across a surface area of 1.3×10^{-9} m^2, the molar flow rate of acetic acid into the sodium nitrite droplet is 7.7×10^{-15} $kmol\ s^{-1}$. As a total of 2.6×10^{-14} kmol must flow into the droplet, this gives a total time for diffusion of 3.4 s.

Diffusion of nitrous acid

In the case of diffusion out of the sodium nitrite droplet, mass transfer occurs from $z_1 = 10$ μm to $z_2 = 68$ μm. Inside the droplet, the dinitrogen trioxide concentration evolves from an initial value of 4 $kmol\ m^{-3}$ ($x_{A1} = 0.068$), to a final value of 0.028 $kmol\ m^{-3}$ ($x_{A1} = 0.00048$). Again, assuming that $x_{A2} = 0$, we obtain a log-mean average molar flux of 9.4×10^{-6} $kmol\ m^{-2}\ s^{-1}$, with a corresponding molar flow rate of 2.9×10^{-13} $kmol\ s^{-1}$. Considering that a total of 2.6×10^{-14} kmol must leave the droplet, we obtain a total time for diffusion of 0.089 s.

Combined diffusion control

Upon linear combination of the above two diffusion steps, we conclude that the total time for diffusion, with rapid chemical reaction, would be approximately 3.5 s. Here, it is predicted that the rate-limiting diffusion step will be that of acetic acid into the sodium nitrite droplets. Intuitively, diffusion out of the sodium nitrite droplets is expected to be the faster of the two steps, due to the presence of a steeper concentration gradient.

For experiments at ambient temperatures, chemical gassing requires around 4,000 s for completion. Even at higher temperatures, around 1,000 s is required. However, if chemical reaction were instantaneous, the process would only take around 4 s due to mass-transfer effects. As such, the earlier approximate calculations suggest that the process is not limited by ordinary diffusion. We will now experimentally examine whether or not this conclusion is justified.

Results and Discussion

Emulsion kinetics

The first gassing experiment was conducted at 25 °C — a temperature near the lower limit commonly encountered in the field. Measurements made at 25 °C may also be readily compared to other literature values obtained under conditions of standard temperature and pressure. The density change with time for this particular test is shown in Figure 3, along with a dashed line indicating the minimum density for complete conversion of all added sodium nitrite to nitrogen gas.

Figure 3 reveals three distinct regimes in the chemical gassing of an emulsion explosive. First, we notice a short lag period, which we propose is largely due to the time required to saturate the aqueous phase with dissolved nitrogen. According to our calculations, a delay of several seconds might also be expected due to molecular diffusion. Second, a kinetic regime is entered into, where a steady decrease in emulsion density is observed. Finally, we witness a plateau regime from around 2,000 s at 25 °C, where the emulsion density begins to level off, ceasing to approach the dashed line indicating complete reaction. Swayambunathan et al.[22] also found limiting conversions during the chemical gassing of emulsion explosives, with their experiments reaching approximately 70% conversion (in comparison, the earlier experiment yielded about 74% conversion). Obviously, one component of this gap between the theoretical and actual final density is due to the amount of produced nitrogen gas dissolved in the aqueous phase of the emulsion. Considering that the solubility of nitrogen in water and oil, respectively, corresponds to 0.0245 and 0.123 m^3 per m^3, the emulsion solubility should be about 0.032 m^3 per m^3, or 0.025 m^3 per g. When solubility is taken into account using this value, the majority of the initial lag period is accounted for. However, nitrogen solubility does not fully account for the total initial production of nitrogen. We believe that the remaining difference is due to reacted thiourea which has not yet undergone decomposition. During a study of thiourea nitrosation under similar conditions to those used here (although in aqueous media), da Silva et al.[25] observed that their reaction solutions retained a distinct yellow color for many hours after reaction had ceased. This was thought to be a result of equilibrium formation of *S*-nitrosothiourea, which is a well known product of thiourea nitrosation.[26] Because the formation of this species is not included in Eq. 1, the observed kinetics are expected to depart from the proposed rate equation as the equilibrium position is approached.

Kinetic mechanism

In this section we examine the kinetic results depicted in Figure 3, based on the assumption that mass transfer is not limiting. From the results of this kinetic study, we will evaluate the validity of our initial assumption. We must first make a conversion from emulsion density to nitrite ion concentration in order to perform a kinetic analysis. This is achieved by calculating the total volume of nitrogen gas created, then converting this value to moles of nitrite ions consumed using the ideal gas law, and assuming that no generated nitrogen gas leaves the system. The total volume of nitrogen gas created is calculated from the change in density, plus the amount of nitrogen dissolved in the emulsion. It was assumed that saturation of the emulsion with nitrogen gas occurred exclusively during the lag period. This conversion from emulsion density to sodium nitrite concentration now allows us to study the intrinsic kinetics of the reaction mechanism. Previously, da Silva et al.[25] determined that chemical gassing in the presence of thiourea proceeded via the nitrosating agent ON^+, based on the results of experiments conducted in aqueous media at typical reagent concentrations found in emulsion explosives. The rate equation derived for nitrosation via ON^+, at identical concentrations to those used in this study, is given as Eq. 4. Integration of this rate equation shows that the reaction kinetics should follow a linear plot between $(-192\ \ln[NaNO_2] + 192\ \ln([NaNO_2] + 0.0052))$ and t, with slope of $0.18k'$ (concentration units of mol L^{-1}). For more details concerning the derivation of this rate equation, consult reference 25. In this reaction mechanism, thiourea initially reacts with ON^+ to produce *S*-nitrosothiourea ($ON^+SC(NH_2)_2$) according to Eq. 5, then deprotonates to yield $ON^+SC(NH^-)(NH_2)$. Finally, this species undergoes *S* to *N* rearrangement to produce $H_2NCSNHNO$, which decomposes to yield nitrogen gas. According to this mechanism, the apparent rate constant k' is equal to $K_5K_6k_7$. K_5 has been measured as 5,000 M^{-1}, while K_6 and k_7 have been estimated as 2.3 10^{-5} M^{-1} and 18.0 s^{-1},[25], respectively

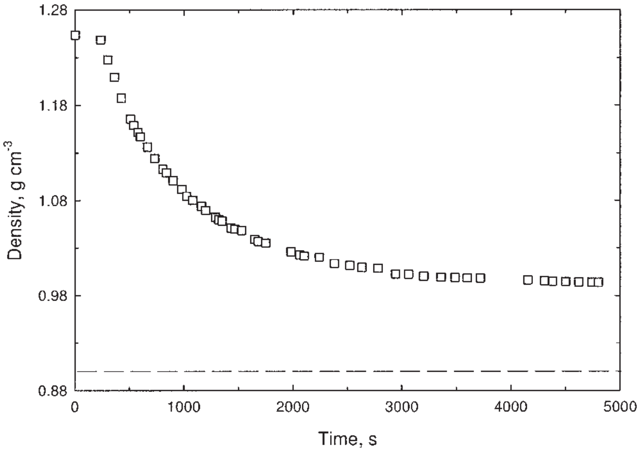

Figure 3. Density change with time for the chemical gassing of an emulsion explosive at 25 °C.

Dashed line indicates theoretical minimum density.

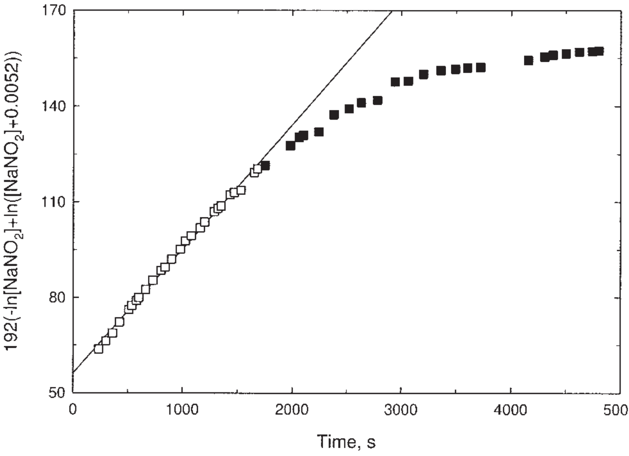

Figure 4. Comparison between experimental results and rate equation for the nitrosation of thiourea by ON^+.

Open squares indicate data to which the integrated rate equation was fit.

$$-\frac{d[NaNO_2]}{dt} = 0.18k'[NaNO_2]([NaNO_2] + 0.0052) \quad (4)$$

$$HNO_2 + SC(NH_2)_2 + H^+ \rightleftharpoons ON^+SC(NH_2)_2 + H_2O \quad (5)$$

$$ON^+SC(NH_2)_2 \rightleftharpoons ON^+SC(NH^-)(NH_2) + H^+ \quad (6)$$

$$ON^+SC(NH^-)(NH_2) \rightarrow H_2NCSNHNO \quad (7)$$

The rate equation for nitrosation via ON^+ is tested in Figure 4. In fitting the rate equation, the initial lag period was excluded from the experimental results by not plotting the zero-time density. Kinetic results from the plateau regime were also excluded, as indicated in the figure. Figure 4 shows that the initial period of reaction is well described by the rate equation proposed by da Silva et al.[25] However, as reaction progresses, and the plateau regime is approached, the observed reaction kinetics begin to deviate markedly from the proposed rate

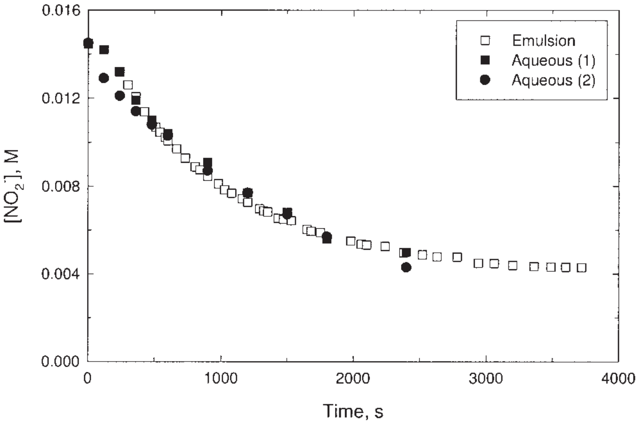

Figure 5. Comparison between gassing reaction in emulsion and in aqueous solution.

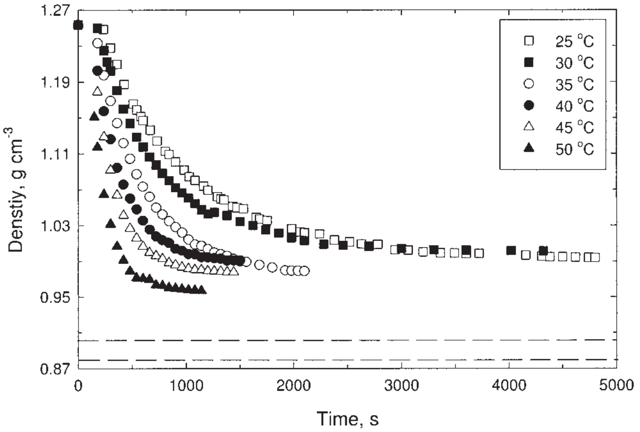

Figure 6. Chemical gassing of emulsion explosive at various temperatures.

equation. During the initial kinetic period, an observed rate equation of 0.0390 s^{-1} is obtained, with a correlation coefficient of 0.997. According to Eq 4, the measured observed rate constant corresponds to $k' = 0.22\ M^{-1}\ s^{-1}$.

Mass-transfer effects

We have compared the kinetic results from the emulsion experiments to the results of previous experiments conducted in aqueous media, at similar concentrations, so as to validate the assumption that the gassing process is controlled by the rate of chemical reaction.[25] The aqueous experiments were performed in a well-stirred reactor, with samples removed periodically and quenched in sodium hydroxide solution. The quenched samples were analyzed for nitrite ion concentration using ion chromatography. Figure 5 shows a comparison of the emulsion and aqueous results.

In Figure 5 we notice that both the aqueous and emulsion experiments return very similar kinetics during the initial stages of reaction. During this period, the emulsion experiment provides a k' value of 0.22 $M^{-1}\ s^{-1}$, while an average k' value of 0.21 $M^{-1}\ s^{-1}$ was reported for the aqueous experiments. In addition, Al-Mallah et al.,[26] measured k' to be 0.2 $M^{-1}\ s^{-1}$ in aqueous media. The similarity between the aqueous and the emulsion rate constants indicates that mass-transfer effects are not significant, as the aqueous experiments were well-mixed and homogeneous. This supports our theoretical finding, and also validates the kinetic approach adopted in analyzing the reaction rate data. Furthermore, we can also conclude that the nitrosation of ammonia is not a dominant mechanism in the chemical gassing of emulsion explosives, as no ammonium nitrate was present in the aqueous experiments.

Activation energy

Chemical gassing experiments were conducted at temperatures of 30, 35, 40, 45 and 50 °C to obtain an activation energy. The measurements for each of these experimental runs are shown in Figure 6, along with the data obtained at 25 °C. Also included in Figure 6 are two dashed lines indicating the minimum densities for complete nitrite conversion at both 25 and 50 °C.

In Figure 6 we notice that at each temperature the measurements fall into the three regions identified at 25 °C. We also observe that the rate of reaction increases markedly with increasing temperature. Despite this increase in rate, the minimum density is not reached by any of the experiments. While the higher temperature experiments do yield lower final densities, this is mainly due to thermal expansion of the gas phase, and not a consequence of any further reaction progress (as indicated in the figure by the dashed lines representing the minimum density for complete nitrite conversion).

The measurements within the kinetic regime were plotted according to the rate law of Eq. 4, as for the experiment at 25 °C. Rate constants (k_{obs} and k') acquired for each temperature are given in Table 1. The data in Table 1 may be used to determine the activation energy of the reaction, by means of an Arrhenius plot. This is illustrated in Figure 7, where $1/T$ is plotted against $\ln k'$, which reveals a good linear relationship. From this linear relationship, we obtain Eq. 8, describing k' as a function of temperature

$$k = 4.42 \times 10^9 \exp\left(\frac{-7080}{T}\right) \tag{8}$$

Equation 8 implies an activation energy of 59 kJ mol^{-1}. Activation energies of this magnitude invariably indicate reaction-controlled kinetics. Also, the lack of curvature suggests that there is no change in the kinetic mechanism with varying temperature. This implies no transition between *N*- and *S*-nitrosation, and no shift in the controlling mechanism from chemical reaction to diffusion control. In aqueous media, da Silva et al.[25] measured an activation energy of 61 kJ mol^{-1} for thiourea nitrosation, which again agrees well with that deter-

Table 1. Observed and Intrinsic Rate Constants at Various Temperatures

Temperature (°C)	k_{obs} ($M^{-1}\ s^{-1}$)	k' ($M^{-1}s^{-1}$)
25	0.039	0.22
30	0.056	0.31
35	0.088	0.49
40	0.12	0.67
45	0.15	0.83
50	0.27	1.5

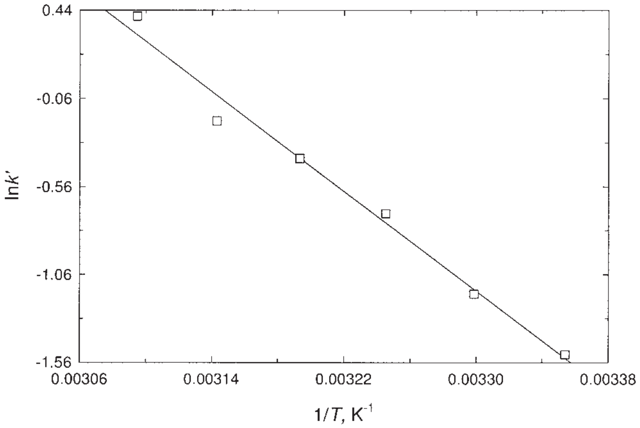

Figure 7. Arrhenius plot for chemical gassing over the temperature range of 25 to 50 °C.

mined here in emulsion, indicating that diffusion control is not significant.

Conclusions

It has been determined, both experimentally and theoretically, that the chemical foaming of emulsion type explosives is controlled by chemical kinetics, rather than molecular diffusion. Chemical gassing was observed to follow three regimes. The first regime was a lag period, arising due to saturation of the emulsion with aqueous nitrogen. Next, a kinetically controlled regime was entered into, followed finally by a plateau regime. Experimental measurements collected within the kinetically controlled regime follow a rate equation suggesting that the nitrosation reaction proceeds by way of the nitrosating agent ON^+. Here, thiourea acts as a substrate, replacing the role of ammonia in the traditional system. The nitrosation of thiourea in emulsion proceeds with an apparent rate constant of $0.22\ M^{-1}\ s^{-1}$ at 25 °C, consistent with previous measurements in aqueous media. The activation energy for thiourea nitrosation was measured to be 59 kJ mol^{-1}, within the temperature range of 25 to 50 °C, indicating that mass-transfer control is not significant. The experiments conducted here in emulsion returned similar reaction kinetics to previous experiments conducted in aqueous media, with respect to the reaction rate, mechanism and activation energy. This provides further evidence that mass transfer does not control the gassing process. Our results also indicate that ammonia plays no major role in the reaction mechanism.

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