Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 225-235

ARC STUDY OF THERMAL STABILITY OF ALKALI METAL ALKOXIDES

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Abstract

Alkali metal alkoxides can be formed by the direct reaction of alkali metals with the corresponding alcohol. Under certain conditions, however, these reactions become dangerous. One of the reasons for the instability build-up in the reaction mixture is related to the electrochemical behaviour of the heterogeneous medium. Another reason is the instability introduced by the simultaneous presence of oxygen and alkali metal atoms in the reagents. Accelerating rate calorimetry is an excellent way to determine safe working conditions for the handling of such compounds. The hazards that are encountered are discussed by means of some examples.

Keywords: accelerating rate calorimetry, alcoholate, alkali metal, alkoxide, thermal stability

Introduction

A kinetic study of the reactions of alkali metals with alcohols reveals that the reaction rate does not undergo a regular change as the reagents are consumed. Strong oscillations in reaction rate occur, the extrema of which can differ by a factor of more than ten (Fig. 1). At the spontaneous end of the reaction, the observed reaction rate can be extremely different for two samples treated under apparently identical conditions (Fig. 2). In general, at the end of the reaction, not more than 50% of the stoichiometric quantity of alcohol has been converted.

Under certain conditions, however, the reaction may become quantitative. This is the reason for a major hazard build-up in the course of such reactions, since they are very exothermic (typically 150–200 kJ mol^{-1}, depending on the alcohol and the alkali metal [1]). Accelerating rate calorimetry (ARC), by its principle, allows slow heating to bring the reaction mixture very smoothly from stable conditions to runaway situations. The simultaneous determination of spontaneous adiabatic pressure and temperature evaluation furnishes information concerning the reasons for instability, and permits an estimation of the limits of safe working conditions.

In a first step, this work describes the results of a thermodynamic and kinetic study of the reactions of alcohols with metallic sodium. The influence of the alcohol concentration in an inert solvent was examined, in order to acquire more information concerning the main reaction mechanisms. Since these aspects are not the aim of this work and have recently been discussed elsewhere [2], merely the highlights will be given here, for a clear understanding of the phenomena described. A second step

1418–2874/99/ $ 5.00

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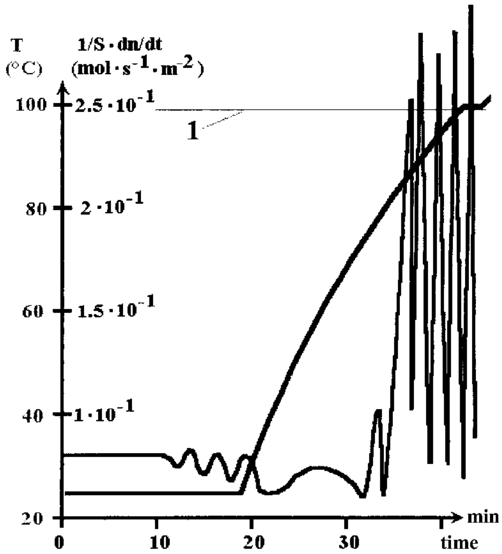

Fig. 1 Sodium reaction rate *vs.* time as function of temperature: 15% mol BuOEtOH, 0.7 g Na, 85% ligroin; 1: Na melting temperature

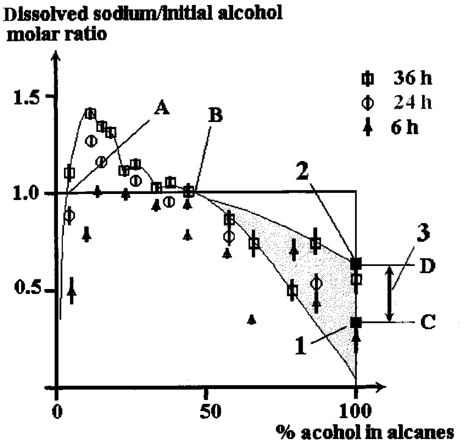

Fig. 2 Solubility of sodium in butoxyethanol *vs.* initial alcohol concentration: A – hyperstoichiometry lower limit; B – hyperstoichiometry upper limit; C, 1 – spontaneous end-point; D, 2 – final end-point; 3 – 25% of initial energy: 300 kJ kg^{-1}, $\Delta T_{ad} \approx 150$ K

consisted in producing sodium alkoxides by the reaction of pure alcohols with metallic sodium, with testing of the thermal behaviour of the final reaction mixtures by ARC. This relates to the essential aim of this work: the demonstration of how such systems can turn into explosive runaway situations and how the ARC technique can provide information concerning the potential hazard level and the limits of the safe work conditions.

Experimental

Thermodynamic and kinetic study

The alcohols used for this study were medium-sized alcohols, containing or not containing heterofunctional oxygen (and sometimes nitrogen) atoms. We chose to compare 1-heptanol, 2-heptanol, 2-butoxy-1-ethanol (butyl cellosolve, glycol monobutyl ether), 3-propoxy-1-propanol, 4-ethoxy-1-propanol and diethyleneglycol monomethyl ether (methyl carbitol). All these alcohols have the same number of non-hydrogen atoms, i.e. a total number of eight oxygen or carbon atoms, and their diffusion kinetics are very similar. The effects of replacing the ether functions by secondary amine functions was also studied. The water contents of all these products were determined by Bizot's coulometric technique in order to verify the absence of water from the reagents. The water to alcohol molar ratio in all the alcohols was found to be less than 0.1%. The solvent used for dilution of the alcohols was rectified ligroin, a mixture of aliphatic hydrocarbons boiling between 120 and 150°C. Its water content was likewise determined by coulometry, and was found to be lower than 8 parts per million.

The metallic sodium was nuclear grade sodium from Pechiney-Metaux Speciaux, preliminarily purified by a segregation-extraction technique in order to lower its potassium content to below 10 part per million by mass [3]. Thermodynamic measurements of the reaction limits of sodium as a function of the alcohol concentration in ligroin were performed in a nickel crucible, the temperature of which was stabilized within ±0.1°C.

Kinetic measurements were carried out by means of a specially designed device (Fig. 3). A continuous flow of solvent was heated by direct contact with a nickel chromium resistor so as to minimize the time constant of the heating device. The outlet temperature was monitored in order to get a good temperature regulation of the sample (within ±0.5°C of the programmed value) whatever the reaction exothermicity might be. The sodium sample was a spherical sample of about 1 g of metallic sodium, obtained by melting and solidification in a 2% butoxyethanol-containing ligroin bath. (The butoxyethanol cleans the surface of the metal sample so that coalescence of the liquid metal occurs spontaneously.) After solidification, the sodium

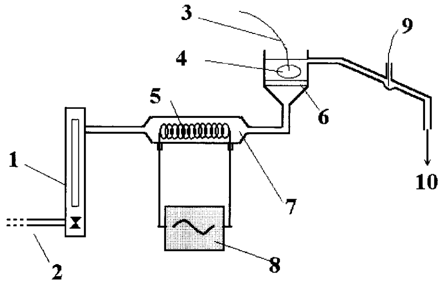

Fig. 3 Experimental device for kinetic studies: 1 – flow rate adjustment and control; 2 – cold solvent inlet; 3 – thermocouple; 4 – sodium sample; 5 – NiCr coil; 6 – coarse sintered glass filter; 7 – solvent heater; 8 – power supply; 9 – to atomic absorption spectrophotometer; 10 – to waste

sample was rinsed three times with ligroin in order to stop the surface reaction with butoxyethanol. The subsequent storage in ligroin allowed the sample surface to remain sufficiently oxygen-free for use during several hours. Sodium concentrations in the organic phase were determined with a Varian AA-6 atomic absorption spectrophotometer.

ARC study

Since the previously mentioned thermodynamic and kinetic studies revealed an appreciable explosion hazard for the described reactions, ARC measurements were carried out in order to establish the relatively safe working conditions. The accelerating rate calorimeter, designed by Columbia Scientific Industries Corporation, allows reaction studies under near-perfect adiabatic conditions. To accomplish this, the sample is introduced in a spherical metallic sample holder (a bomb). The wall thickness of the bomb defines the upper limit of the inner maximum pressure. However, thick bomb walls results in a lowering of the adiabaticity coefficient Φ, defined as

$$\Phi = m_\mathrm{s}C_{\mathrm{p_s}}/(m_\mathrm{s}C_{\mathrm{p_s}} + m_\mathrm{b}C_{\mathrm{p_b}})$$

where m_s and m_b are the masses of the sample and of the bomb, respectively, and $C_{\mathrm{p_s}}$ and $C_{\mathrm{p_b}}$ are the heat capacities of the sample and of the bomb, respectively.
The bomb is placed inside a nickel-plated copper jacket equipped with thermocouples and heating elements to produce a uniform jacket temperature and to maintain zero temperature difference between the sample holder and the jacket. Heating is carried out stepwise until the self-heating rate of the sample becomes detectable. Once a self-heating rate is detected above a preselected threshold, the sample is automatically maintained under adiabatic conditions for the duration of the exotherm. From the recorded data, numerous relationships may be determined, such as adiabatic temperature rise, temperature of maximum self-heating rate, time to maximum self-heating, self-heating rate *vs.* temperature, pressure *vs.* temperature, pressure rate *vs.* temperature, or pressure rate *vs.* temperature rate.

The experiments were performed with alcoholates containing 50 g l^{-1} (about 2 mol l^{-1}) sodium in initially pure alcohols (7–10 mol l^{-1}, depending on the molecular mass). Some products were studied for industrial applications and are therefore confidential. Accordingly, besides the description of the stability of sodium butoxyethanolate and methylcarbitolate, merely some typical results concerning them will be mentioned here in order to demonstrate the power of the ARC technique in safety studies of some observable behaviour of industrial interest.

The working conditions for the described experiments were as follows: spherical Hastelloy-C bombs, with 0.8 mm wall thickness and 10 ml volume, for pressure up to 103 500 kPa. The specific heat of the bomb material was 0.42 J (g K^{-1}). The start temperature was 80°C, and the end temperature 375°C. The slope sensitivity was 0.02 K min^{-1}. The heat step was set at 5.00, the data step at 1.00, and the calculation step at 0.20. The cool temperature was 40.00°C, with the radiant heat fraction at 1. The pressure stop was set at 63 000 kPa and the wait time to 10 min. The sample mass was about 3.5 g.

Results and discussion

At first sight, the reaction of sodium alcoholate formation seems to be a very simple one:

$$\mathrm{Na} + \mathrm{ROH} \longleftrightarrow \mathrm{RONa} + 1/2\mathrm{H}_2$$

In fact, this reaction is a heterogeneous reaction involving at least three phases: the conductive metal, the insulating solvent (even when saturated with alcoholate, its resistivity is higher than 20 MΩ cm) and the gaseous phase involving evolved hydrogen. Alcoholate precipitation sometimes leads to the formation of a supplementary solid phase. Problems of nucleation and growth of the gas phase, and charge distribution over the solvent-metal interface, strongly alter the behaviour of the reaction.

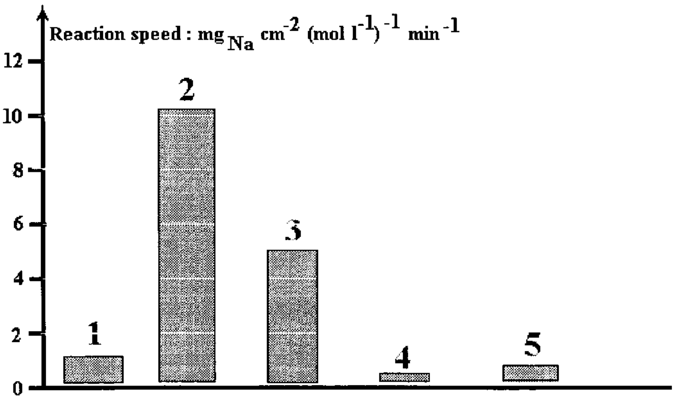

Fig. 4 Influence of ether position on alcohol function reactivity: 1 – 1-heptanol; 2 – butoxyethanol; 3 – 3-propoxy-1-propanol; 4 – 4-ethoxy-1-butanol; 5 – 5-methoxy-1-pentanol

Figure 1 shows the reaction rate as a function of time under varying temperature conditions. After an initiation period of about 10 min, the sodium sample starts oscillation kinetics with 15% butoxyethanol diluted in ligroin. These oscillations are disturbed by the starting of a temperature ramp. Once the temperature has reached a level near the melting point of the alkali metal, strong oscillations take place, leading to instantaneous reaction rate fluctuations by a factor of 4. Since that actual reaction signal is damped by the time constants of both the reaction cell and the atomic absorption spectrometer, a factor of about 10 can be estimated for the instantaneous rate variations of the sample reaction. All the studied alcohols exhibited similar behaviour. However, the reaction rates of alcohols bearing an ether function were higher than those of alcohols without such a heterofunctionality. For example, butoxyethanol reacted 20 times faster than 1-heptanol under the same conditions (Fig. 4). Figure 6 shows the reactivities induced by several heterofunctionalities near the active alcohol function. The main conclusion is that the alcohol function reactivity enhancement due to a heterofunction bearing a non-bonded electron pair is most important when the heterofunction is close to the alcohol function. Reactivity en-

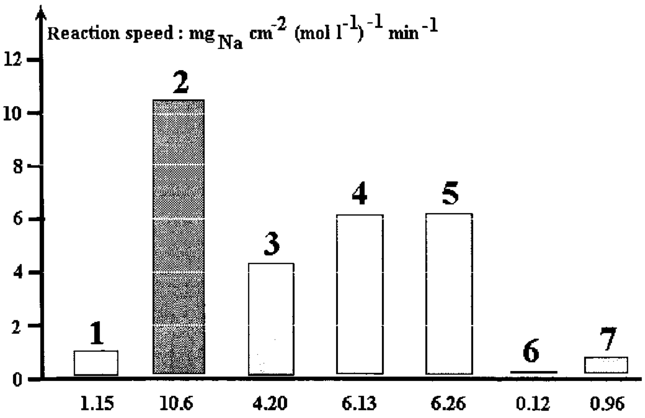

Fig. 5 Influence of heterofunctionality on alcohol function reactivity: 1 – heptanol; 2 – butoxyethanol; 3 – 2-butylaminoethanol; 4 – 2-(N-butyl-N-methyl)amino-1-ethanol; 5 – 2-(N-methyl-N-propyl)amino-1-ethanol; 6 – *n*-heptanol and heptylamine 1:1; 7 – *n*-heptanol and heptylamine 4:1

hancements due to ether functions (Fig. 4) are more important than those observed for amine functions in the same position (Fig. 5). Addition of an amine group into an alcohol did not increase its reactivity (Fig. 5). This is clear evidence of the importance of the non-bonded electron pairs in the first adsorption step required for the reaction of an alcohol with sodium.

Figure 2 shows the corresponding thermodynamic aspects: the sodium to initial alcohol (butoxyethanol) molar ratios of the solutions are plotted *vs.* the alcohol concentration in the organic reagent. Three typical regions appear in this plot:

1. For an alcohol concentration below 5% vol. alcohol in ligroin (point A, Fig. 2), the reaction never reaches the expected stoichiometric conversion rate. Since the ligroin components and the reacting alcohol have similar molecular masses, the percentage volume is near the molar percentage. This hypostoichiometry is stronger for heterofunction-bearing alcohols.

2. Between 5 and 50% vol. alcohol, the reaction conversion rate exceeds the stoichiometric value (horizontal line in Fig. 2). For an alcohol such as heptanol, without an additional heterofunctional oxygen atom, the conversion rate never exceeds the expected stoichiometry. This is due to the possibility for alkali metals to react not only with the hydrogen atoms of alcohol functions, but also with the ether function, the non-bonded electron pairs of the oxygen of which are a site where cationic sodium can be fixed, leading to breaking of the closest less stable oxygen-carbon bond. With heterofunctionless alcohols, such a reaction is not possible. Thus, for ether function-containing alcohols, sodium will not only yield alcoholate formation, but also result in exothermic partial decomposition reactions breaking the ether oxygen-carbon bonds.

3. For alcohol concentrations exceeding 50% vol. (beyond point B in Fig. 2), the final conversion rates are lower than the expected stoichiometric value. Moreover, the reaction end-points yield randomly distributed conversion rates. This is true for all the studied alcohols.

These experimental facts can be explained by taking into account the amphiphilic character of the studied alcohols. These aspects were discussed in a recent communication [2]. They are due to the formation of a charged double layer across the metal-solvent interface. The negative charge build-up in the metallic phase is compensated by a positive charge build-up in the organic phase. However, these charge build-ups result in strong changes in the electrical potential of the phases in which they take place. For a capacitor, the relation between capacitance *C*, electrical charge *Q* and electrical potential *U* is $U=Q/C$. The chemical system is steered in the same way: the lower the electrical capacitance of the considered phase, the more important its electrical potential variations. Thus, during the double layer formation, the electrochemical potential of sodium decreases, whilst the electrochemical potentials of all species contained in the organic phase increase. As soon as the protonated alcoholate present at the interface starts nucleation and growth of hydrogen bubbles, deprotonation occurs, discharging the negative charges stored in the alkali metal, its electrochemical potential hence rising again to its initial value. This will result in relaxation kinetics leading to sawtooth reaction rates as shown in Fig. 6. Several authors mention such behaviour for similar systems [4–6]. The heavy lines in this Figure show the changes in the chemical potentials of the various compounds in the system with increasing conversion rate. The fine lines indicate the corresponding electrochemical potentials of all concerned species. The reaction will stop first when the sum of the chemical potentials of the initial products is reached by the rising sum of the chemical potentials of the final products. The first time this can occur is at point A in Fig. 4. Under the evolution conditions as revealed by this Figure, the nor-

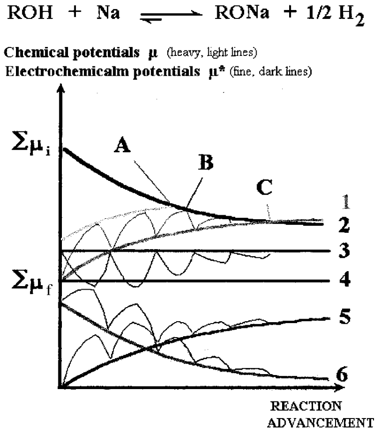

Fig. 6 Evolution of potentials during sodium alcoholate formation: A – first possible stop, B – first spontaneous stop, C – ultimate reaction end, 1 – final products, 2 – initial products, 3 – Na, 4 – H_2, 5 – RONa, 6 – ROH

mal spontaneous observable end-point will be at point B. After this spontaneous step, however, on discharge of the interfacial double layer giving rise to the electrical contribution of the total potential of the reacting species, the reaction can start again, the last end-point of which will be reached at the equilibrium point C in Fig. 6. The gap between A and C in Fig. 6 corresponds to the vertical amplitude of the dashed area observable beyond an alcohol to ligroin ratio of 50% in Fig. 2. Thus, for pure alcohols reacting with sodium, it is easy to reach spontaneous end-points at the midpoint between C and D (Fig. 2). Discharge of the interfacial layer will restart the reaction and allow it to reach the end-point D. Stirring, which results in breaking of the alkali metal droplets, can be a factor leading to the apparent discharge of the interfacial layer: increase in the specific surface of the metal will enhance its electrical capacity, so that the corresponding electrical potential will be lowered. Since discharge of the capacity is an autocatalytic phenomenon, the reaction will go to completion on vigorous stirring. Such stirring can be started by a local hot-point generating hydrogen bubbling. Consequently, such behaviour can be the starting point of explosive runaways. Under the described conditions, even the half-amplitude between C and D in Fig. 2, which is very commonly observed as a spontaneous end-point in pure alcohols, represents about 0.2 stored potential molar ratio evolution. Since the studied alcohols are 7 to 8 mol l^{-1} when pure, this value is near 1.5 moles,

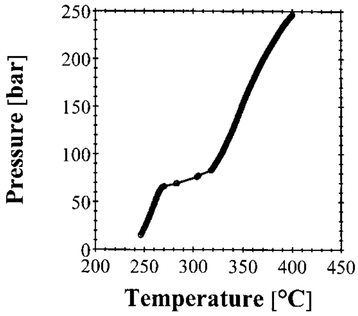

Fig. 7 Adiabatic decomposition of Na-butoxyethanolate (50 g l^{-1}). Pressure *vs.* temperature

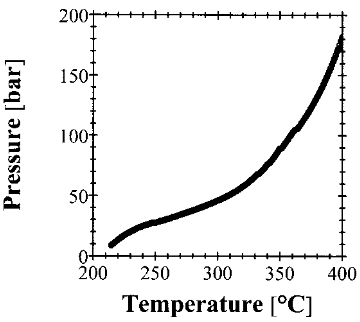

Fig. 8 Adiabatic decomposition of Na-methylcarbitolate (50 g l^{-1}). Pressure *vs.* temperature

corresponding to a potential energy content of about 300 kJ kg^{-1}. The corresponding adiabatic temperature rise of the medium is consequently about 150 K. This value is high enough to bring the system up to temperatures inducing exothermic decompositions reactions.

Thus, ARC studies are required to determine the conditions for which the system can be operated under relatively safe conditions. Figure 7 depicts the thermal decomposition of sodium butoxyethanolate, by means of the plot of pressure *vs.* temperature. Two steps appear clearly. In comparison, the same plot for sodium methylcarbitolate reveals that this alcohol, containing a number of ether functions, starts to decompose at lower temperatures. Although not so apparent as in the previous example, two steps are also observable here. Their overlap results in a nearly continuous evolution of pressure *vs.* temperature (Fig. 8).

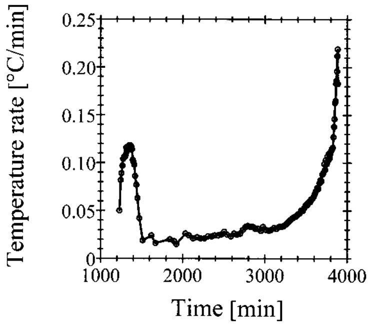

Fig. 9 Adiabatic decomposition of Na-butoxyethanolate (50 g l^{-1}). Temperature rate *vs.* time

Another interesting representation is given by the plot of temperature rate *vs.* time (Fig. 9): in such a representation, the two previously mentioned steps of butoxyethanolate decomposition are readily observed. The important time gap between the first decomposition and the final explosive runaway is clearly seen. The pressure rate *vs.* temperature rate plot (Fig. 10) demonstrates that the gas formation and heat evolution are not simply correlated during the thermal decomposition of sodium bu-

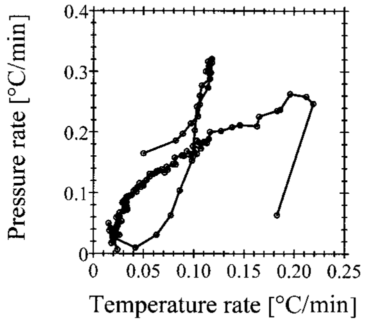

Fig. 10 Adiabatic decomposition of Na-butoxyethanolate (50 g l^{-1}). Pressure rate *vs.* temperature rate

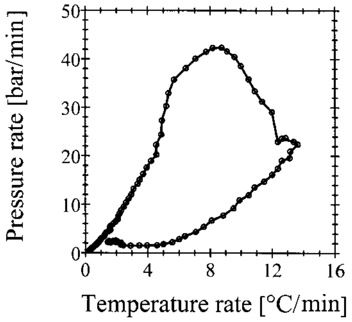

Fig. 11 Adiabatic decomposition of alcoholates containing several oxygen atoms. Pressure rate *vs.* temperature

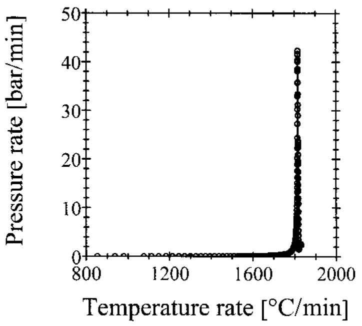

Fig. 12 Adiabatic decomposition of alcoholates containing several oxygen atoms. Pressure rate *vs.* time

toxyethanolate. This relatively stable product can be compared with the following one, the composition of which is confidential (Fig. 11). A comparison of the scales of Figs 10 and 11 indicates that in the latter case pressure and temperature rates are achieved that are about 100 times higher than those for the previously described butoxyethanolate. Such a compound leads to extremely sensitive working conditions, the hazards of which appear clearly in Fig. 12, in which the pressure rate is plotted *vs.* time: after a long initiation period, an extremely fast runaway occurs. The 150 K mentioned above as the potential adiabatic temperature rise due to the energy accumulation by the uncompleted reaction would here be easily able to bring the system into dangerous working conditions if effective fast cooling down were not foreseen.

Conclusions

The reactions of sodium with alcohols are very complex, involving a first adsorption step at the alkali metal surface. They yield of the reaction depends on the electrochemical charge build-up at the metal-reagent interface. The breaking of the metallic phase into droplets may result in an apparently completed reaction starting up again. The corresponding enthalpy content that becomes free in this way is able to give rise to an adiabatic temperature rise of the system of more than 150 K. ARC studies indicate that this temperature rise, starting from the melting temperature of sodium, is considerable enough to bring the system into a dangerous runaway situation. The potential hazard depends strongly on the shape of the molecules concerned, and the presence of oxygen heterofunctions able to enhance the runaway rates of the system by a factor of 100 once its decomposition has begun.

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