

THE APPLICATION OF THE REACTION CALORIMETRY TO INVESTIGATE REACTIONS INVOLVING UNSTABLE COMPOUNDS

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The RC1 calorimeter revealed itself a suitable instrument to obtain information about safety and mechanisms involved in the reaction between cyclohexanecarboxylic acid (AEB) and oleum. A previous hypothesis about the existence of an unstable intermediate was confirmed and its heat of formation was calculated. The heat of sulphonation related to undesirable by-products production and the heat of protonation of AEB with H₂SO₄ were also evaluated. Therefore, it was possible to distinguish the reactions involved in the process and, through their thermal behaviour, to determine the limit conditions to avoid the by-products formation.

Keywords: reaction calorimetry, unstable intermediate

Introduction

For several years, the reaction calorimetry was known to be suitable to study chemical processes in order to obtain information on safety, kinetics and scale up [1-4]. Many advantages may be taken of this technique: to evaluate the thermal behaviour of potentially dangerous reactions, to determine limit conditions to safe operations and to make provision on effects of errors and anomalous events, etc.. However, the reaction calorimetry could also be useful for targets other than industrial safety. In fact, if the reactions involved release or absorb some energy, it is possible to use heat for monitoring the evolution of the system, thanks to the relationship between chemical and thermal conversion. Therefore, it is also possible to follow the formation of compounds that are relatively stable only inside the reacting system, but not isolable and recognizable by usual analysis.

This peculiarity was exploited in order to get better information on the phenomena involved in the reaction between cyclohexanecarboxylic acid (AEB) and oleum. In past years, many studies and hypotheses have been made [5-17]. The formation of a relatively stable intermediate only within the reaction system

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was supposed: it could react with nitrosylsulphuric acid to produce caprolactam and, in the meantime, it seemed to be responsible for the co-production of undesirable sulphonic acids like α -sulphocyclohexanecarboxylic acid (ACCS) and benzenesulphonic acid (ABS) [Fig. 1a]. Until now, this intermediate had not been isolated and only speculations had been made about its nature. One of the most supported ideas refers to a mixed anhydride between AEB and SO_3 [Fig. 1b] because of the existence of analogous isolable anhydrides, which derive from SO_3 and aliphatic acids and give off the α -sulphocarboxylic acids when heated [18]. However, these studies were not able to make a kinetic correlation between the supposed intermediate and the sulphonate by-products. This fact did not allow a prediction in order to minimize their productions.

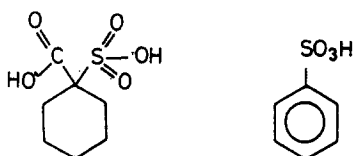


Fig. 1a The main by-products: α -sulphocyclohexanecarboxylic acid and benzenesulphonic acid

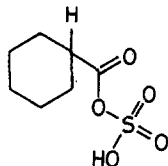


Fig. 1b The mixed anhydride between cyclohexanecarboxylic acid and SO_3

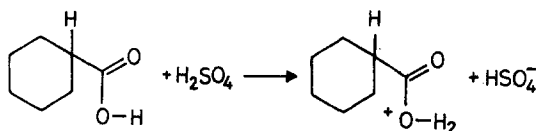


Fig. 1c The protonation of AEB by H_2SO_4

Though the real structure of the intermediate was not confirmed, the reaction calorimetry gave the possibility of studying this system, due to the exothermicity of the main reactions involved, and it was possible to support the hypothesis about the existence of a reaction between cyclohexanecarboxylic acid and SO_3 , kinetically distinguishable with respect to the sulphonate by-products.

Experimental

The experiments were done in a 2-liter reaction calorimeter (RC1-METTLER), working under isothermal conditions. Cyclohexanecarboxylic acid was

dissolved with *n*-heptane to make stirring more effective. The stirrer was a glass propeller working at 600 rpm. Thermocouples measured continuously the temperature of jacket and mass reaction. After the beginning and at the end of the reaction, the global heat transfer coefficient through the reactor wall (U) was calculated by means of calibrations:

$$U = Q_c / A * (T_r - T_j)$$

T_r = reactor temperature °C, T_j = jacket temperature °C, A = exchange area m^2 , Q_c = calibration power W: all these being known.

Oleum was added to the reaction mass under controlled conditions: temperature 45°C, dosing time 50 min. The final molar ratio AEB/SO₃ was equal to 3. Aging time was 3 hours. The temperature range examined was between 30° and 80°C. Oleum concentrations were tested from 0 to 63.7% and *n*-heptane concentrations from 0 to 45% were tested. The reaction system was kept under N₂ atmosphere.

During and after the reactions, samples were drawn and analysed by HPLC, after hydrolysis and neutralization.

In order to calculate instantaneous (Q_r) and integral (Q_{tot}) heat production, some contributions were kept into consideration: measured heat flow through the reactor wall (Q_{flow}), heat accumulation rate by the reaction mass (Q_{acc}), heat flow due to dosing (Q_{dos}), heat flow through the reactor cover (Q_{loss}). Finally, the global expression for calculation was:

$$Q_{tot} = \int_0^t Q_r dt = \int_0^t (Q_{flow} + Q_{acc} + Q_{dos} + Q_{loss}) dt$$

where:

$$Q_{flow} = UA * (T_r - T_j) / W$$

$$Q_{acc} = m_r * C_{pr} * dT_r / dt / W$$

$$Q_{dos} = (dm_d / dt) * C_{pd} * (T_r - T_d) / W$$

$$Q_{loss} = \alpha * (T_r - T_a) / W$$

T_d, T_a = temperature of dosed material and room temperature /°C

m_r, m_d = reaction mass and dosing mass /Kg

C_{pr}, C_{pd} = reaction mass and dosing mass specific heat /J·Kg⁻¹·K⁻¹

α = specific reaction coefficient /W·K⁻¹

dm_r/dt = dosing rate /Kg·h⁻¹

dT_r/dt = rate of temperature change /°C·h⁻¹

The heat production is related to the reaction rate (r) through the expression:

$$Q_r = \sum_i r_i * \Delta H_i * V$$

Discussion

Initial experiments were done at temperatures below 40°C, adding oleum 45%. From the heat flow shape [Fig. 2], it was noted that heat production was started only with dosing, remained constant and then went rapidly to zero. It was interpreted as a fast and exothermic reaction involving the formation of the intermediate. It could also be said that the reaction rate was controlled by dosing. HPLC analysis showed no by-product either after dosing or after aging. However nothing else besides AEB was found, confirming the intermediate instability. From the point of view of safety, no relevant problem emerged: the adiabatic rise, assuming the entire reaction occurred without heat exchange, was about 55°C, not enough to get the system near to decomposition temperatures, found over 170°C (ARC tests).

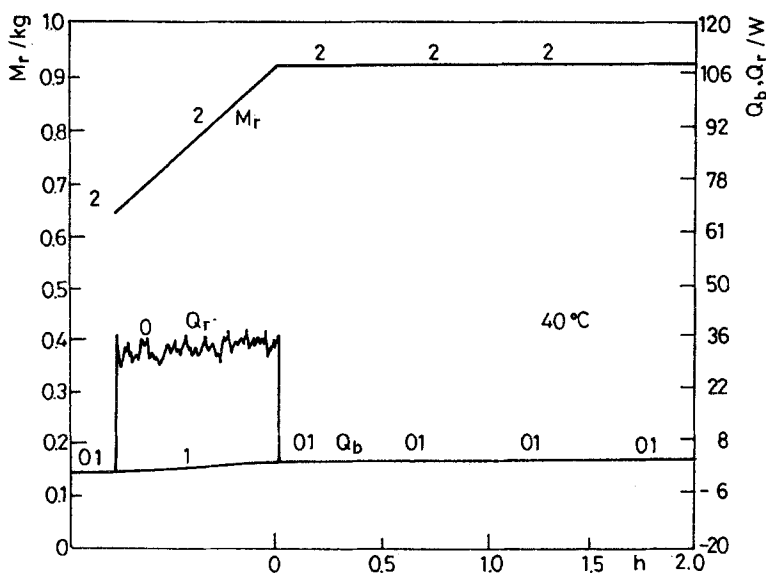


Fig. 2 The typical heat flow curve for a low temperature reaction with oleum 45%

The influence of the temperature on the reactions had been analysed in the range from 40° to 80°C, with steps of 10°C, others parameters being constant. Results are shown in Fig. 3: from 40° to 70°C, no great influence was found during the dosing, without relevant effects on the heat flow. However, as far as aging was concerned, the higher the temperature, the more modified were the curves. Finally, at 80°C, a new exothermic phenomenon started to affect also the dosing, as it could be seen from the visible distortion of the heat flow curve. Moreover, with respect to the aging period, it could also be noted that the heat production was maximum in the first 30 minutes and decreased slowly over time.

On the basis of thermal data, two different phases were recognizable: the first one, during the dosing of oleum, characterized by fast reactions, was exhausted right after and probably connectable with the AEB protonation and the intermediate formation. The latter phase, essentially the aging period, was characterized by slower exothermic reactions, connected with the undesirable sulphonates production, strongly affected by temperature. Therefore, it was possible to distinguish the main reactions involved in the process and, through their thermal behaviour, to determine the limit conditions to avoid the by-products formation, competitive with the intermediate formation above 50°C. HPLC analysis confirmed such hypotheses: α -sulphocyclohexanecarboxylic acid (ACCS) and benzenesulphonic acid (ABS) were found, whose amounts were directly dependent on temperature, as can be seen in Fig. 4. It can be noted that, at 80°C, the conversion in ACCS, with respect to SO₃, was 50% at the end of dosing already.

It is also relevant to note that the ratio ACCS/SO₃ was found equal to 0.5 also after 100 hours aging and the operating temperature was only able to affect the rate at which the constant value was reached. The existence of such a plateau

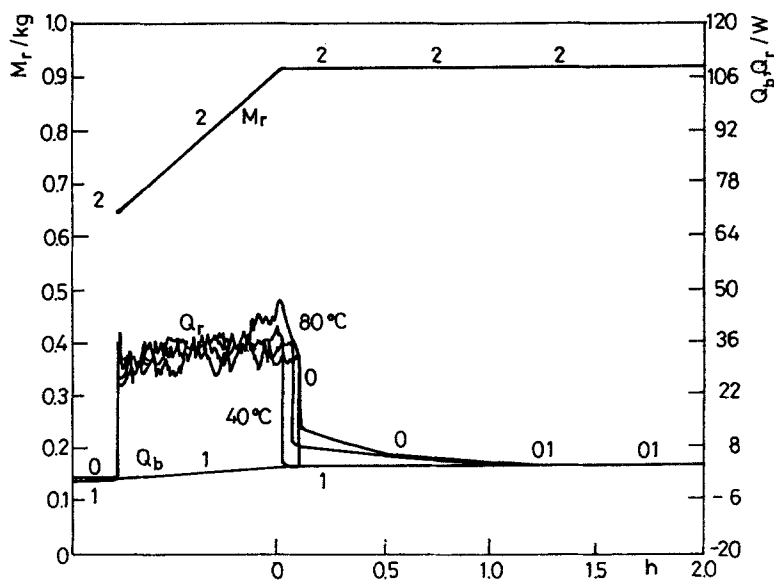


Fig. 3 The effect of the temperature on the heat flows in the range between 40° to 80°C

forced some authors [6] to suppose some equilibria between the intermediate, in the form of mixed anhydride, and the sulphonates. However, other tests, done within the plateau conditions, showed that neither an increase nor a decrease in temperature changed the initial composition, as one should expect as a result of changes in equilibria due to change in temperature. Therefore, the mechanism seems to be much more complicated.

In order to obtain more information, the effect of changes in oleum concentration in the range from 30% to 63.7%, keeping the moles of SO_3 constant was studied. The experiments were done at 70°C , to ascertain a considerable forma-

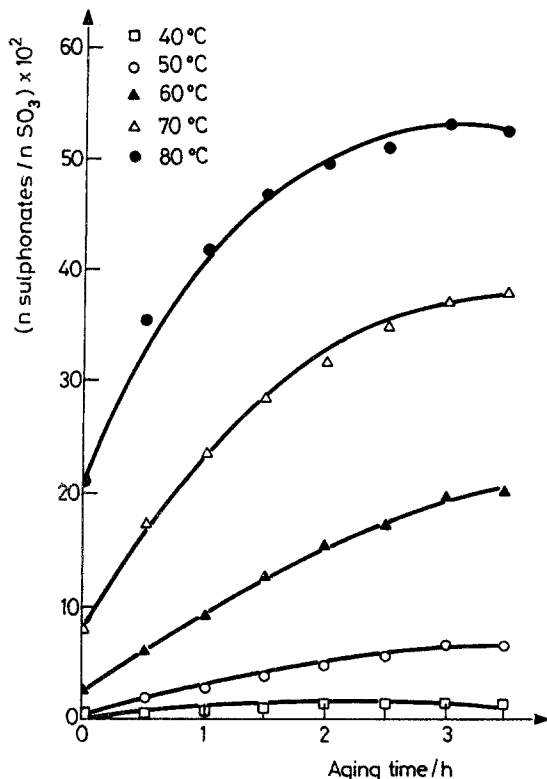


Fig. 4 The conversion on sulphonates with respect to SO_3 in the range between 40° to 80°C

tion of sulphonates. The results are shown in the Figs 5 and 6. As far as the heat flows were concerned, no great change was found, but the total heat production, during the dosing, was reversely related to the oleum concentration. Variations during the aging were difficult to evaluate with reasonable accuracy, because of RC1 sensitivity limits already reached after 30 minutes aging. HPLC analysis showed that the sulphonates production was directly related to oleum concentration, but, above oleum 45%, no great differences were detected.

The possibility of an influence by *n*-heptane, except for its usefulness in making mixing and final separation easier, was analysed. The range between 0% to 45% of solvent with respect to AEB was tested. The operating temperature was 70°C and oleum 45% was added. The results are shown in Figs 7 and 8. Neither heat flows nor integral heats showed relevant changes due to the solvent. Conversion value in by-products with respect to SO_3 , gave evidence of direct depen-

dence with *n*-heptane percentage. In any case, above 15%, the overlapping of heat flow curves indicated no more effects. This behaviour seemed to confirm no relevant effects, other than the ones already known.

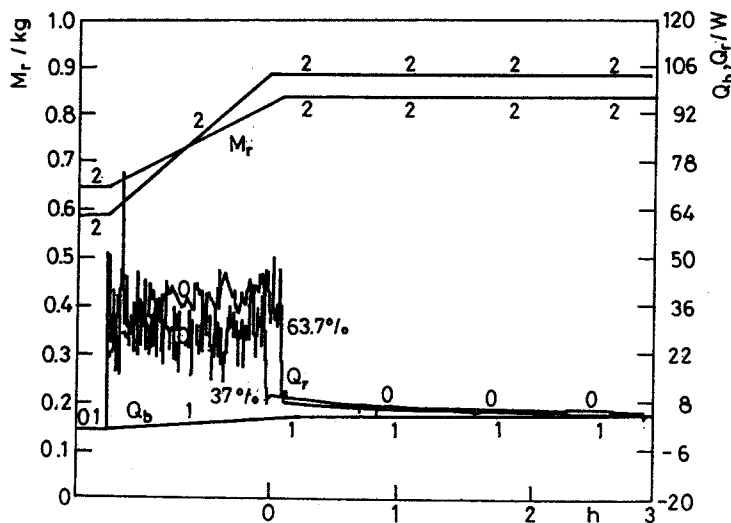


Fig. 5 The effect of oleum concentration on the heat flows in the range between 37 and 67.3%

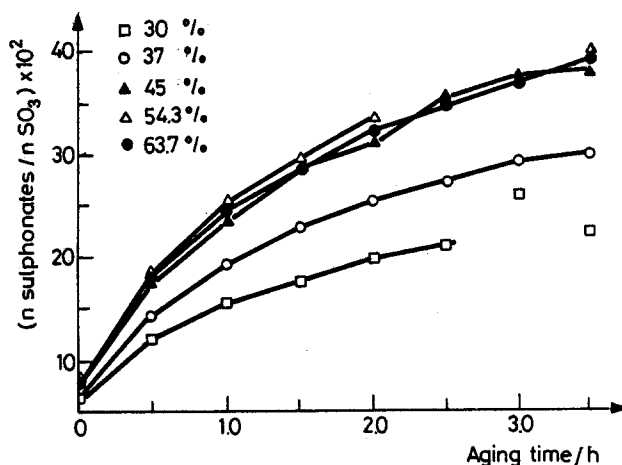


Fig. 6 The conversion on sulphates with respect to SO_3 in the range of oleum concentration between 37 and 67.3%

To calculate the heat of reaction for the formation of the intermediate, supposed to be the mixed anhydride between SO_3 and cyclohexanecarboxylic acid, experiments at temperatures below 40°C were used, conditions of absence of by-products being guaranteed. On the basis of the heat flow shape, SO_3 was sup-

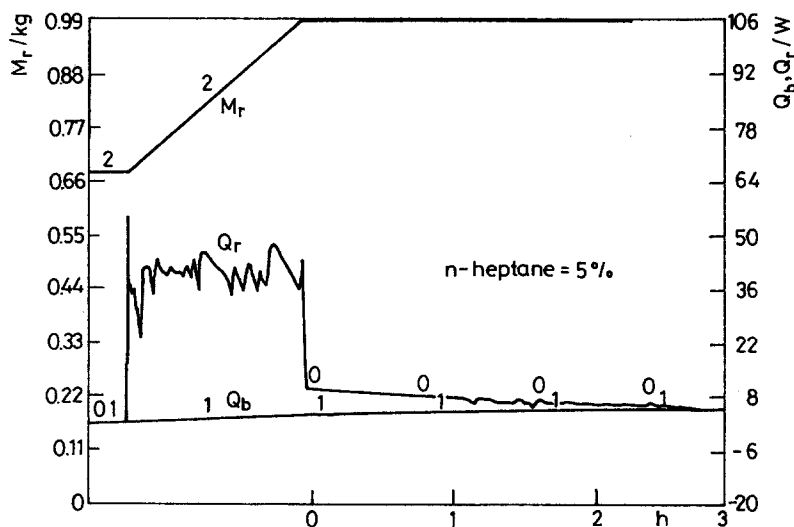


Fig. 7 The heat flow curve at 70°C, oleum 45% and *n*-heptane 5%

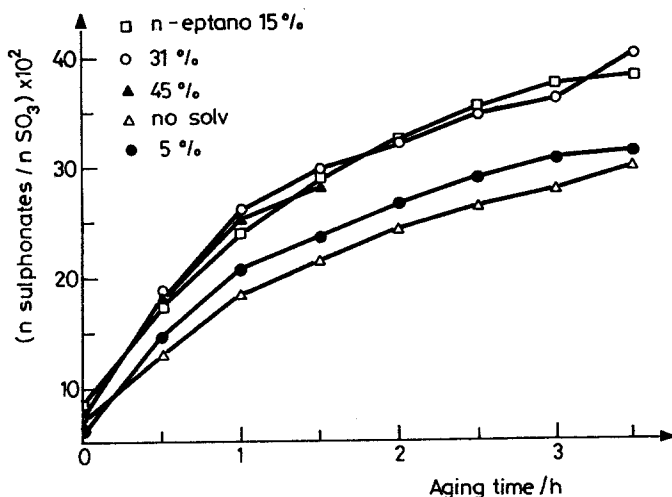


Fig. 8 The conversion on sulphonates with respect to SO_3 in the range of *n*-heptane between 0 to 45%

posed to react completely. The first estimation was -15 kcal/mole of SO_3 . Tests were conducted to evaluate the contribution of interaction between AEB and H_2SO_4 , in order to eliminate it. Different ratio AEB/ H_2SO_4 , related to oleum used before, were tested. H_2SO_4 was added and other operating conditions were not varied. A fast exothermic reaction, lasting only during dosing, was detected. The

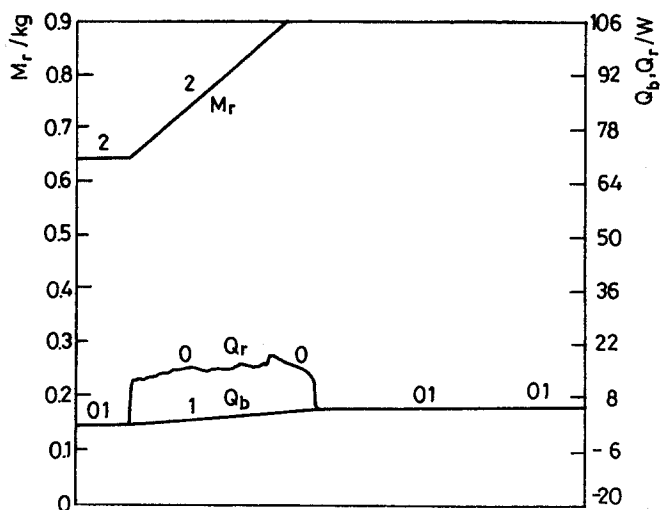


Fig. 9 The heat flow curve for the reaction between AEB and H₂SO₄ 100%

heat flow was three times less than that from oleum tests [Fig. 9] and the calculated heat of reaction was -3.3 kcal/mole of H₂SO₄. This thermal behaviour could be related to the protonation of cyclohexanecarboxylic acid by sulphuric acid [Fig. 1c], as many authors supposed [5]. That could partially justify the larger amount of heat developed during dosing in experiments with more dilute oleum, because of the larger amount of H₂SO₄ able to protonate AEB in excess. By subtracting the heat of protonation, the heat of reaction for the formation of the intermediate became -12 kcal/mole of SO₃. The heat of sulphonation was calculated using only data of the first hour after dosing, to minimize errors. As a matter of fact, many reactions, not distinguishable from a kinetic point of view, were occurring. Moreover, all the hypotheses of mechanisms involved species not isolable or characterizable. The value was estimated to be approximately -13 kcal/mole of sulphonates (ACCS+ABS).

Conclusion

Reaction calorimetry is a suitable instrument not only for industrial safety applications, but also for obtaining information regarding exothermic reactions involving products not easily detectable. For the reaction between AEB and oleum, it was possible to distinguish the main reactions involved in the process, to determine limit conditions for avoiding by-products formation. It was also possible to

estimate the heats of formation for those reactions by putting them in relation to mechanisms hypothesized by previous research.

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Zusammenfassung — Das RC1 Kalorimeter erwies sich als ein geeignetes Instrument, um Informationen über Sicherheit und Mechanismen bei der Reaktion von Cyclohexancarbonsäure (AEB) und Oleum zu gewinnen. Eine bereits bestehende Hypothese über die Existenz eines instabilen Zwischenproduktes konnte bestätigt und dessen Bildungswärme berechnet werden. Weiterhin wurde auch die Sulphonierungswärme bezogen auf die Entstehung von unerwünschten Nebenprodukten und die Protonierungswärme von AEB durch H_2SO_4 ermittelt. Es ist deshalb möglich, die einzelnen Reaktionen innerhalb dieses Prozesses über ihr thermisches Verhalten voneinander zu unterscheiden, um die Grenzbedingungen zur Vermeidung der Bildung von Nebenprodukten zu ermitteln.