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Thermochimica Acta 386 (2002) 65–72

thermochimica acta

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The thermal stability of ethyl diazoacetate

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Received 23 July 2001; received in revised form 20 August 2001; accepted 20 August 2001

Abstract

Ethyl diazoacetate (EDA) is an important organic chemistry synthon, but its use as an industrial intermediate is limited due in part to the safety concerns associated with its instability and high reactivity. In a continuing effort to understand the risk of employing EDA as an industrial reagent, the thermal stability of EDA was studied. Reported are the results of accelerating rate and differential scanning calorimetry (DSC) experiments. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ethyl diazoacetate; Thermal stability; Accelerating rate calorimetry; Differential scanning calorimetry

1. Introduction

Ethyl diazoacetate (EDA) is an important two-carbon synthon for organic chemistry [1–13], but its use as a large-scale, industrial commodity is limited due to safety concerns. The material safety data sheet [14] indicates that this reagent is shock sensitive, flammable and toxic. EDA is also known to be chemically reactive [1–13], thermally sensitive [15] and has been reported to decompose upon heating or distillation [16,29]. In a continuing effort [17–23] to understand the risk of employing EDA as an industrial reagent, accelerating rate calorimetry [24–26] and differential scanning calorimetry (DSC) [27] experiments were completed. Reported are the results of these tests.

2. Results

2.1. Accelerating rate calorimetry (ARC)

The accelerating rate calorimetry results for various concentrations of EDA are summarized in Table 1. The measured curves for each experiment employing increasing concentrations of EDA are shown respectively in Figs. 1–4. The data indicates that self-heating starts within a range of 55–100 °C at concentrations ranging from 11 to 97 wt.%. The maximum self-heating rate ranges from 0.300 °C/min with 11% EDA in toluene to 128 °C/min with 97% EDA. Measured maximum pressure rates were as high as 2280 psi/min. Entry 2 details the results of an experiment in which the sample was held at 40 °C for 48 h before completing the ARC test. The calculated heat of reaction appears to be proportional to the concentration of the EDA. Gas analysis of the decomposition headspace from 97% EDA indicated the major

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PII: S0040-6031(01)00760-2

Table 1
ARC tests of EDA

Entry	EDA (wt.%)	Solvent	Origin of EDA	Adiabatic temperature rise (°C)	Onset decomposition temperature (°C)	Maximum self-heating rate (°C/min)	Heat of reaction (kJ/kg)[a]
1	11	Toluene	Synthesized[c]	43	100	0.35	178
2	11	Toluene	Synthesized[c](48 h hold)	47	70	0.25	180
3	31.6	Toluene	Aldrich[b]	117	68	3.5	516
4	97	–	Aldrich[b]	105	55	130	1560

[a] Value corrected for phi factor. See Section 3.
[b] See [14].
[c] See [22,23].

Table 2
Experimental conditions and DSC tests results

Test	20% EDA[a]	40% EDA[a]
DSC scanning rate (°C/min)	5.0	5.0
Sample weight (mg)	3.5	3.7
EDA (wt.%)	20	40
Temperature (°C) onset	98	101
Heat of reaction (kJ/kg)	306	602

[a] See [28].

products were carbon dioxide (45%), ethane (16%), and nitrogen (21%). It is reported that high boiling esters are also formed [16,29].

2.2. Differential scanning calorimetry (DSC)

Two heat flux DSC experiments were completed studying toluene solutions of EDA. The experimental conditions and key results are summarized in Table 2. The measured curves are shown in Figs. 5 and 6, respectively. The data indicates that self-heating started at approximately 100 °C. The heat of reaction appears to be proportional to the concentration of EDA.

3. Discussion

Analysis of the accelerating rate calorimetry data suggests that the detected onset temperature is relatively insensitive to concentration; however, the results clearly indicate that the maximum temperature rise rate is significantly affected by dilution. Maximum temperature rise rates ranging from 0.300 °C/min for 11% EDA in toluene to 128 °C/min for 97% EDA were observed. The accelerating rate calorimetry data show that self-heating is experimentally determined at a temperature of 55–100 °C and is approximately proportional to the EDA concentration. The final temperature varied from 155–185 °C. The adiabatic temperature rise, which is a measure for the heat of reaction, is calculated as the difference between the final temperature and the onset temperature of self-heating. Thus, it follows that the adiabatic temperature rise for EDA decomposition is within the range of 43–117 °C and is approximately proportional to the EDA concentration.

In order to calculate the heat of reaction corresponding to the measured adiabatic temperature rise, a correction has to be made for thermal inertia, the so-called phi factor. The phi factor or factor of thermal inertia corrects for the fraction of reaction heat that is required to heat the sample vessel. It is defined as

$$\phi = 1 + \frac{m_v}{m_s}\frac{C_{p,v}}{m_s C_{p,s}}$$

where ϕ is the factor of thermal inertia or phi factor; m_s the mass of sample (kg); $C_{p,s}$ the specific heat of sample (J/kg); m_v the mass of bomb (kg); $C_{p,v}$ the specific heat of bomb [J/kg].

By using this estimation, the heat of reaction of an 11% solution of EDA (Table 1, entry 1) is calculated to be 178 kJ/kg. This implies that the final temperature corrected for thermal inertia of the reaction might become 189 °C, provided that no sequential reactions occur that increase the temperature range. The calculated heat of reaction for other concentrations is recorded in Table 1. In all cases, it appears that the heat of reaction is proportional to the concentration of the EDA.

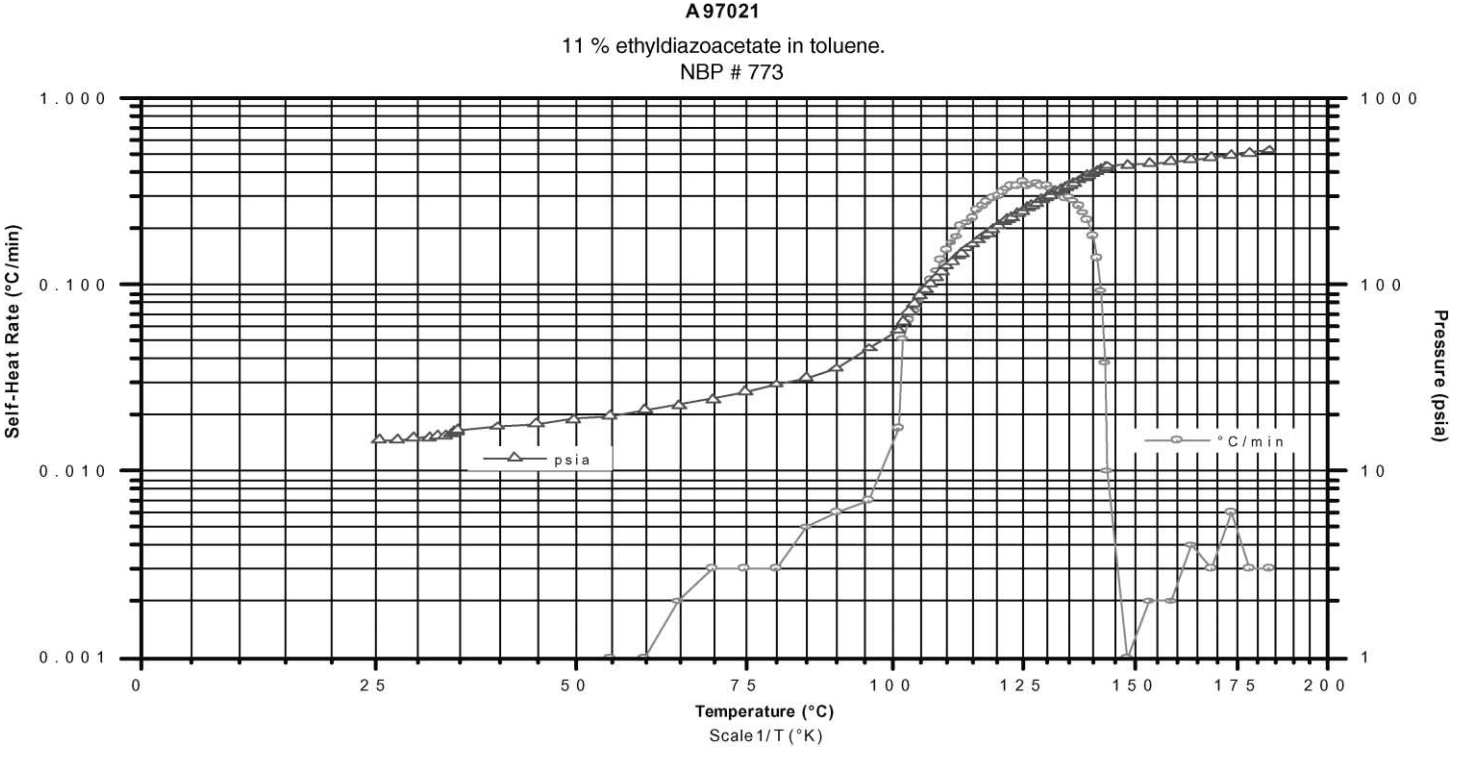

Fig. 1. ARC curve for 11 wt.% EDA in toluene.

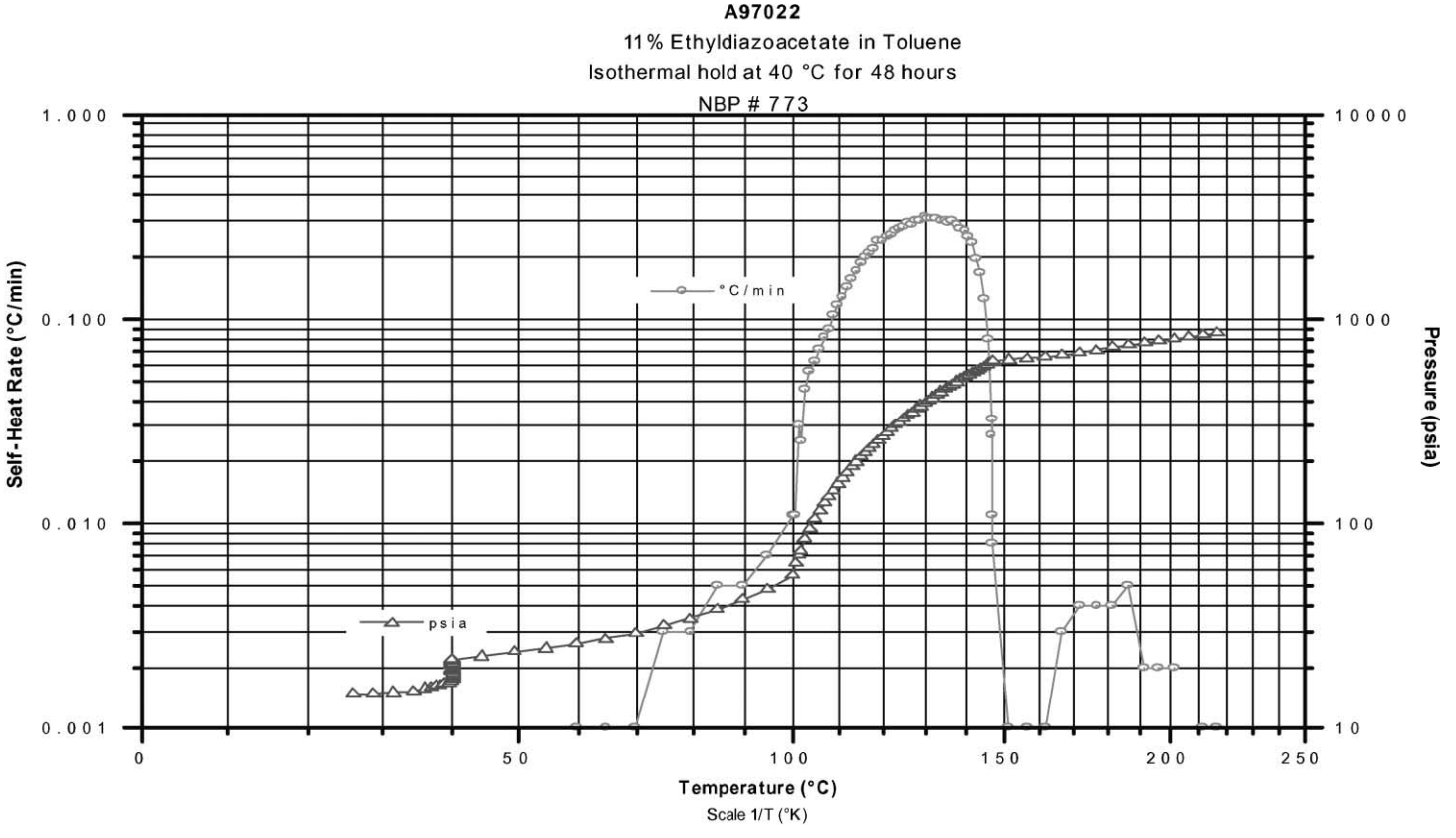

Fig. 2. ARC curve for 11 wt.% EDA in toluene after an isothermal hold of 40 °C for 48 h.

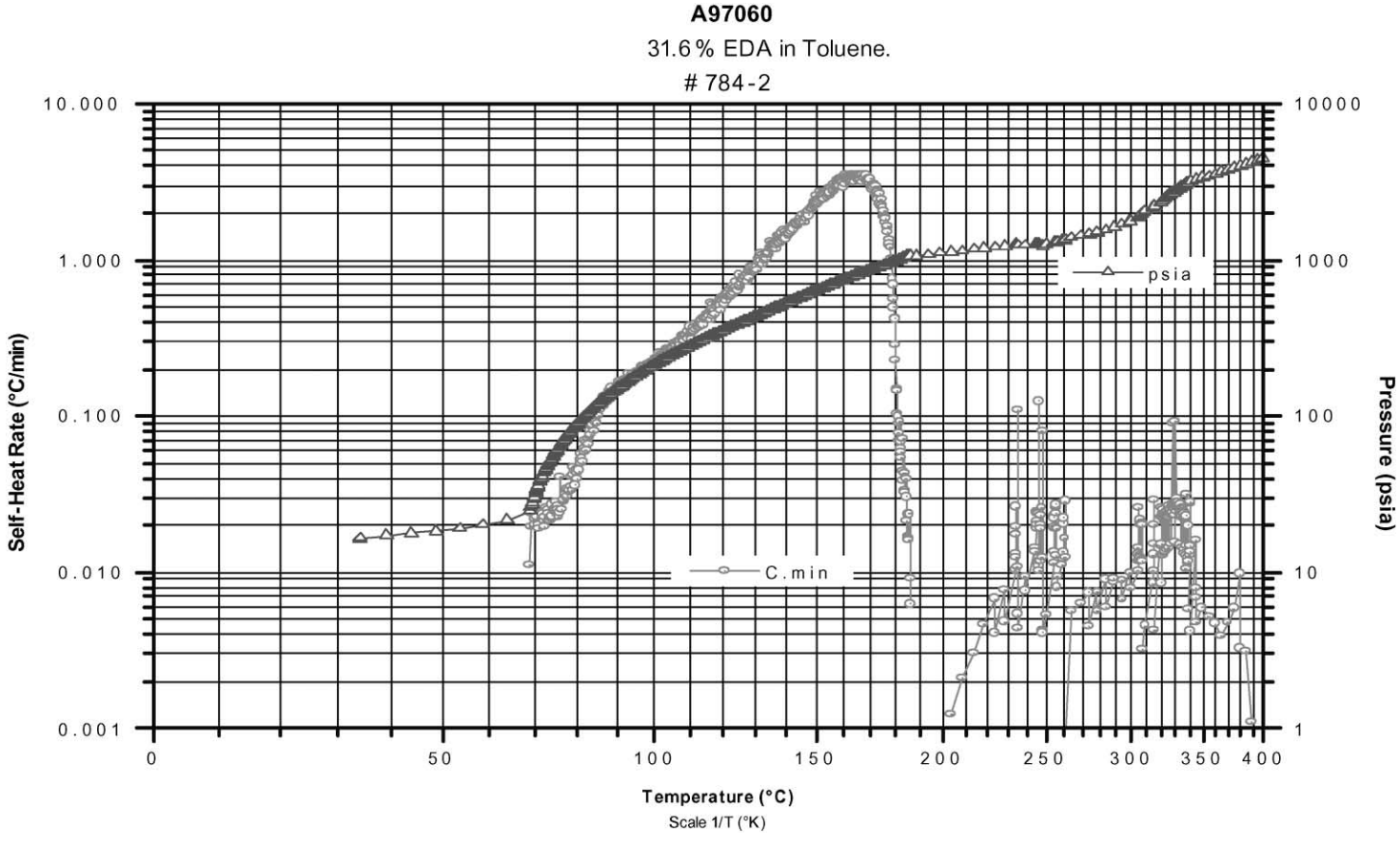

Fig. 3. ARC curve for 31.6 wt.% EDA in toluene.

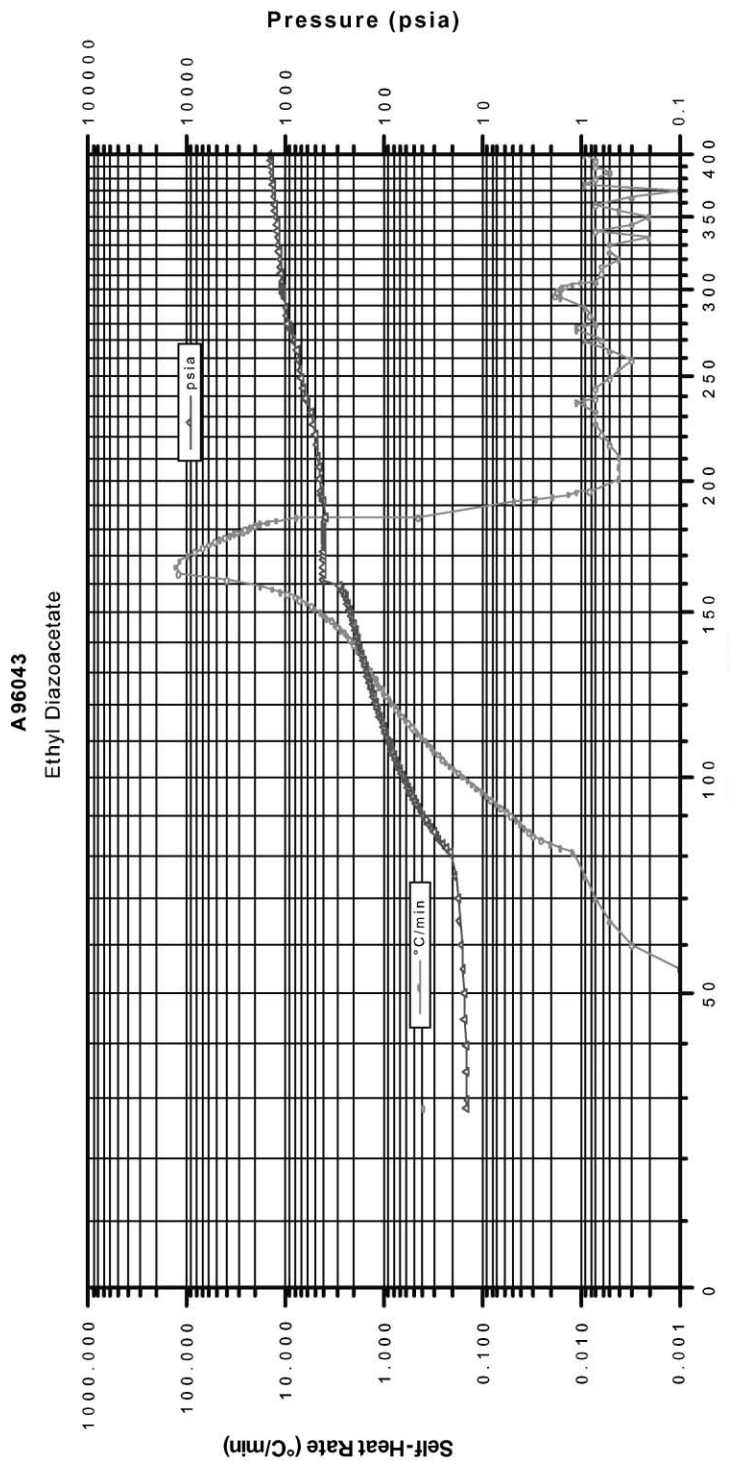

Fig. 4. ARC curve for 97 wt.% EDA in toluene.

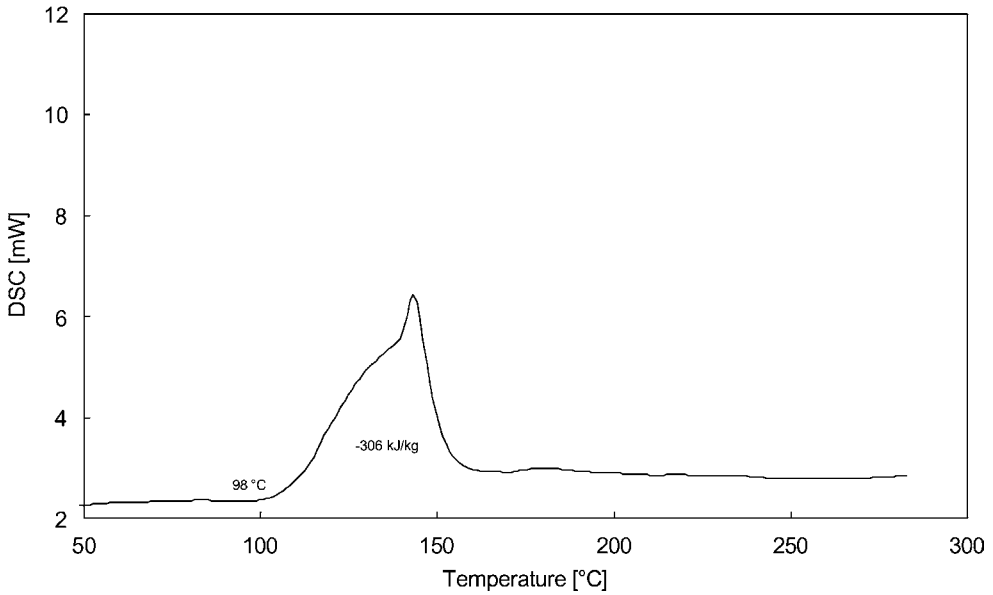

Fig. 5. DSC curve for 20 wt.% EDA in toluene.

Further analysis of the stability characteristics of EDA by DSC showed that the detected onset temperatures in both experiments were in good agreement with the results obtained in the ARC experiments. However, since the detected onset temperature is an equipment dependent parameter (affected by the accuracy or detection limit of the equipment), scaling of the onset temperature must be regarded as highly unreliable.

Heat of reaction using DSC again showed good proportionality to the concentration of EDA. A heat of

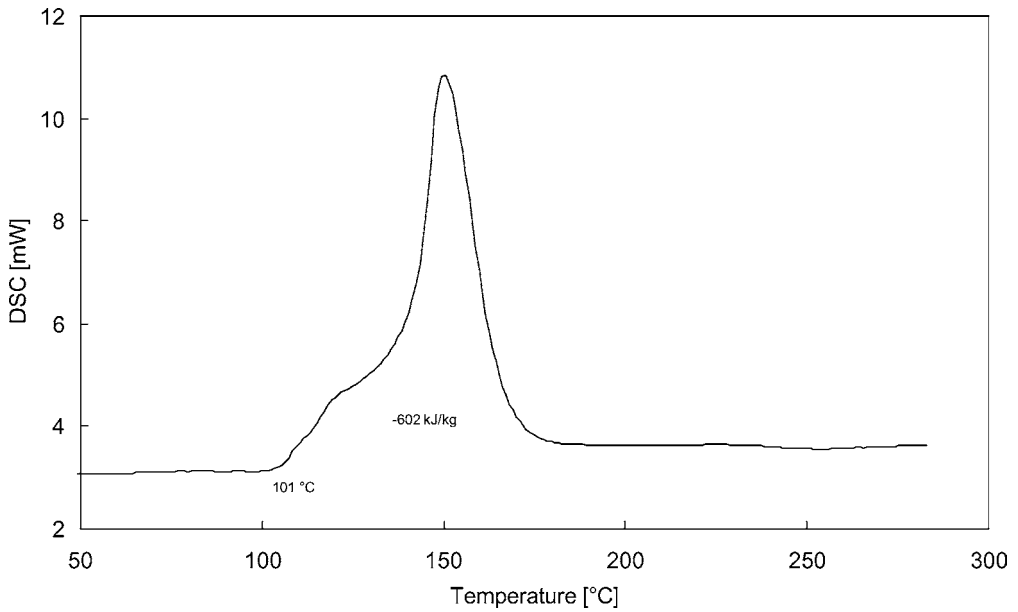

Fig. 6. DSC curve for 40 wt.% EDA in toluene.

reaction of 168 kJ/kg was calculated for a solution with an EDA concentration of 11% in toluene. This value is in good agreement with the heat of reaction calculated from the corresponding ARC experiment (178 kJ/kg) with the same EDA concentration.

The measured curves in the DSC experiments show the same non-symmetric characteristics. This indicates that the decomposition of EDA does not proceed by a simple *n*th order process. The decomposition more probably proceeds by a complicated series or sequence of reactions. The gas analysis data from the ARC study may support this observation.

4. Conclusion

Thermal stability test for various concentrations of EDA were completed. The results indicate that the EDA onset temperature is approximately 100 °C and not significantly impacted by dilution. The maximum temperature rise rate is significantly affected by dilution ranging from 0.3 °C/min for 11% EDA in toluene to 128.5 °C/min for 97% EDA. The results of DSC correlate well with the accelerating rate calorimetry. Employing either calorimetric method indicates that the heat of reaction for decomposition is proportional to the EDA concentration.

References

[1] M.P. Doyle, Acc. Chem. Res. 19 (1986) 348.
[2] M.P. Doyle, Chem. Rev. 86 (1986) 919.
[3] G. Mass, Top. Curr. Chem. 137 (1987) 75.
[4] J. Adams, D.M. Spero, Tetrahedron 47 (1991) 1765.
[5] A. Padwa, S.F. Hornbuckle, Chem. Rev. 91 (1991) 263.
[6] A. Padwa, K.E. Krumpe, Tetrahedron 48 (1992) 5385.
[7] E.A. Shapiro, A.B. Dyatkin, O.M. Nefodov, Russ. Chem. Rev. 62 (1993) 447.
[8] A. Padwa, D.J. Austin, Angew. Chem. 106 (1994) 1881.
[9] A. Padwa, D.J. Austin, Angew. Chem. Int. Ed. Engl. 33 (1994) 1797.
[10] T. Ye, M.A. McKervey, Chem. Rev. 94 (1994) 1091 and references cited therein.
[11] D.J. Miller, C.J. Moddy, Tetrahedron 51 (1995) 10811.
[12] C.J. Moody, C.N. Morfitt, Synthesis 17 (1998) 1039.
[13] S. Kanemasa, T. Kanai, T. Araki, E. Wada, Tetrahedron Lett. 40 (27) (1999) 5055.
[14] Aldrich Chemical Company, Milwaukee, WI 53201-9358, USA.
[15] M. Regitz, W. Bartz, Chem. Ber. 103 (5) (1970) 1477.
[16] N.E. Searle, Org. Synth. Coll. 4 (1963) 424.
[17] J.D. Clark, Therm. Anal. Appl. 28 (2000) 346–351.
[18] J.D. Clark, A.S. Shah, J.C. Peterson, K.M. Gorgan, S. Camden, Thermochimica Acta 367/368 (2001) 75.
[19] J.D. Clark, Therm. Anal. Appl. 27 (1999) 119–124.
[20] J.D. Clark, A. Shah, in: Proceedings of the 9th RC User Forum on the USA Scientific and Technical Program, Marco Island, FL, 27 October 1998.
[21] J.D. Clark, in: Proceedings of the American Institute of Chemical Engineers National Conference, Miami Beach, FL, 20 November 1998.
[22] A.S. Shah, J.D. Clark, Y. Ma, J.C. Peterson, L. Patelis, US Patent No. 6,025,492 (2000).
[23] A. Shah, J.C. Peterson, J.D. Clark, Y. Ma, J. Levine, US Patent Disclosure 38-21 (15071) (December 1997).
[24] S.K. Camden, Monsanto Analytical Sciences Center Report, June 1997. Columbia Scientific Industries, Accelerated Rate Calorimeter employed to obtain experimental data.
[25] Accelerating Rate Colorimeter Operating Manual, Columbia Scientific Industries, CSI Part Number 851-9001.
[26] D.I. Townsend, J.C. Tow, Thermochim. Acta 37 (1980) 1.
[27] Differential scanning calorimetry test were performed by R.J.A Kerten, A.H. Heemskerk, TNO Prins Maurtis Laboratory Report, February 1998, TNO Prins Maurits Laboratory, Lange Kleiweg 137, 2280 AA Rijswijk, The Netherlands.
[28] Ethyl diazoacetate was supplied by Sigma–Aldrich Chemie B.V., Zwijndrecht, The Neatherlands (purity was 97.4% for lot number 08891 and 96.1% for lot number 12573).
[29] M.J. Leku, Cah. Notes Doc. 91 (1978) 313.