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EVALUATION OF THE ACTIVATION ENERGY FOR THE OLIGOMERIZATION OF ETHYLENE USING A MICROREACTOR IN A DTA

L. M. Razo, V. Mayagoitia and G. Etienne

Instituto Mexicano del Petróleo, México 14. D.F.

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The theoretical considerations and the experimental data to calculate the activation energy of the ethylene oligomerization using a microreactor in a differential thermal analyzer are presented.

Experimental

The experiments were carried on in a Differential Thermal Analyzer, Fig. 1, with the following characteristics:

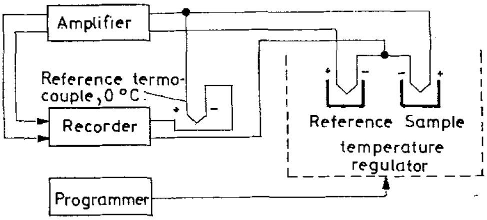

Fig. 1. Block scheme of the differential thermal analyzer

Equipment: DTA Du Pont, Model 900 S.N. 3211

Sensitivity	0.4 – 0.004 mV/in
Operation temperature	20 – 1500 °C
Linear heating rate	0.5 – 20 °C/min
Thermocouples, references and sample	Pt, Pt-13% Rh

Sample preparation

The vials Fig. 2, with or without catalyst *A* or *B* as shown in Fig. 3, are outgassed by means of a vacuum system at pressures of 10^{-2} torr, Fig. 3. After the system is evacuated for 3 or 4 hours, ethylene is introduced and pressure is monitored with a manometer (*F*). With stopcock (*E*) closed, one of the vials is

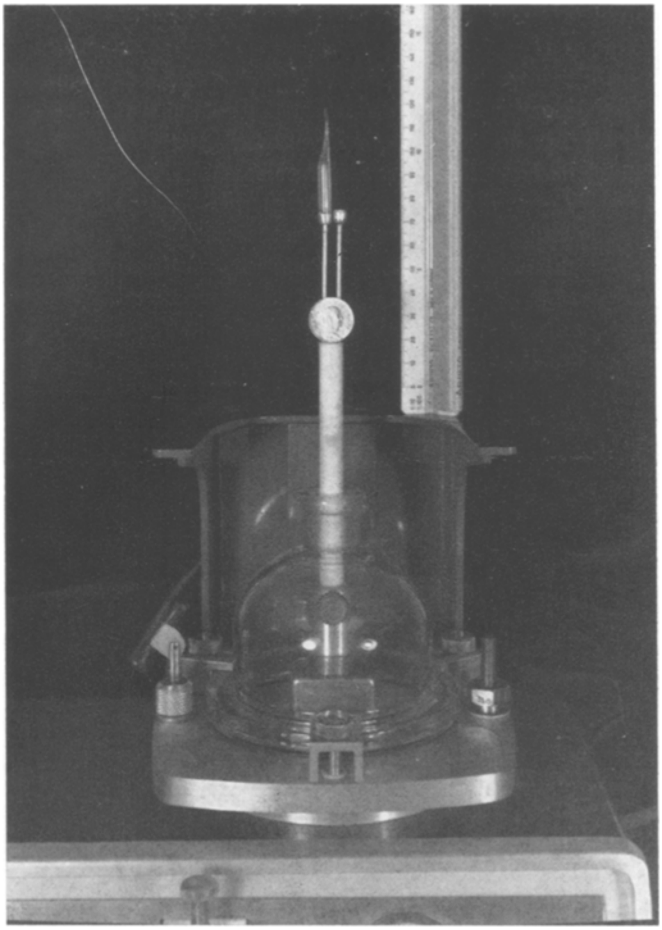

Fig. 2. Differential thermal analyzer

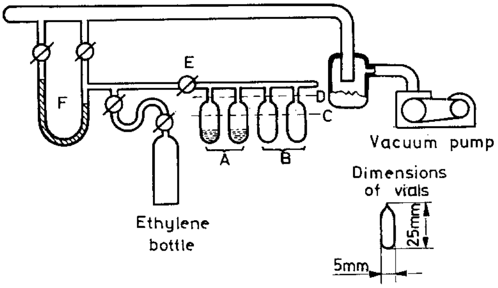

Fig. 3. Sample preparing installation

introduced inside a Dewar flask containing liquid nitrogen up to level (*C*) and ethylene is condensed inside the vial. The capillary tube that connects the vial to the system is sealed by means of a torch; once the vial is out of the vacuum system and reaches room temperature, it is ready for DTA.

The ethylene employed was PEMEX polymerization grade with a purity superior to 99.9% and with ethane as major contaminant.

Theoretical considerations

It is possible to calculate the activation energy from the experimental data obtained from the DTA curve for a particular reaction that occurs inside the vial.

The heat generated by the reaction per unit time is:

$$q = \frac{dQ}{d\theta} = r\Delta H_r = Ae^{-E/RT_M} F \Delta H_r \cdot \tag{1}$$

The heat generated by the reaction per unit time can also be written as:

$$\frac{dQ}{d\theta} = mc_v \left(\frac{dT_M}{d\theta} - \frac{dT_R}{d\theta} \right) \tag{2}$$

$$\text{denoting} \frac{dT_R}{d\theta} \text{ by } v_R \tag{3}$$

$$\frac{dT_M}{d\theta} = \frac{dT_M}{dT_R} \cdot \frac{dT_R}{d\theta} = \frac{dT_M}{dT_R} v_R \tag{4}$$

then,

$$\frac{dQ}{d\theta} = mc_v \left(\frac{dT_M}{d\theta} - \frac{dT_R}{d\theta} \right) = mc_v v_R \left(\frac{dT_M}{dT_R} - 1 \right) \tag{5}$$

$$\frac{dT_M}{dT_R} - 1 = \frac{d(\Delta T)/dT_M}{1 - \frac{d(\Delta T)}{dT_M}} \cdot \tag{6}$$

Therefore,

$$\frac{dQ}{d\theta} = mc_v v_R \left[\frac{d(\Delta T)/dT_M}{1 - \frac{d(\Delta T)}{dT_M}} \right] \cdot \tag{7}$$

From Eqs (1) and (7), it can be deduced that:

$$Ae^{-E/RT_M} F \Delta H_r = mc_v v_R \left[\frac{d(\Delta T)/dT_M}{1 - \frac{d(\Delta T)}{dT_M}} \right] \tag{8}$$

$$\text{letting } C = \frac{A \Delta H_r F}{mc_v v_R} \tag{9}$$

$$Ce^{-E/RT_M} = \frac{d(\Delta T)/dT_M}{1 - \frac{d(\Delta T)}{dT_M}} \cdot \qquad (10)$$

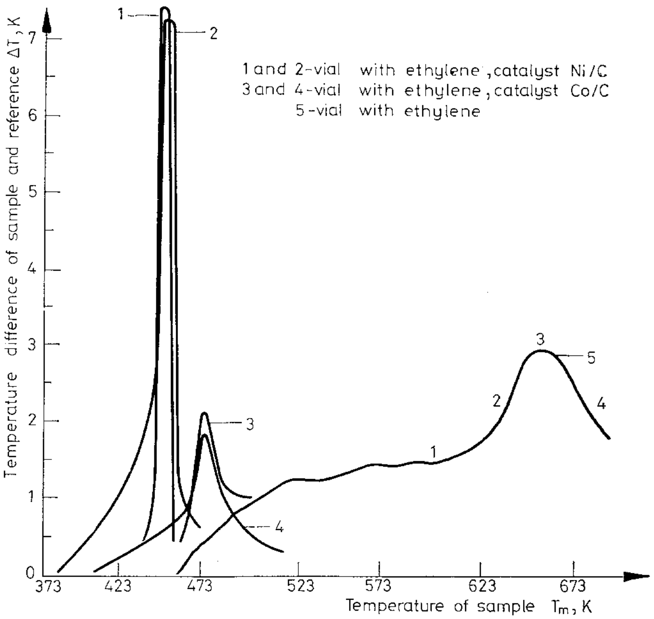

Fig. 4. DTA curves for the oligomerization of ethylene

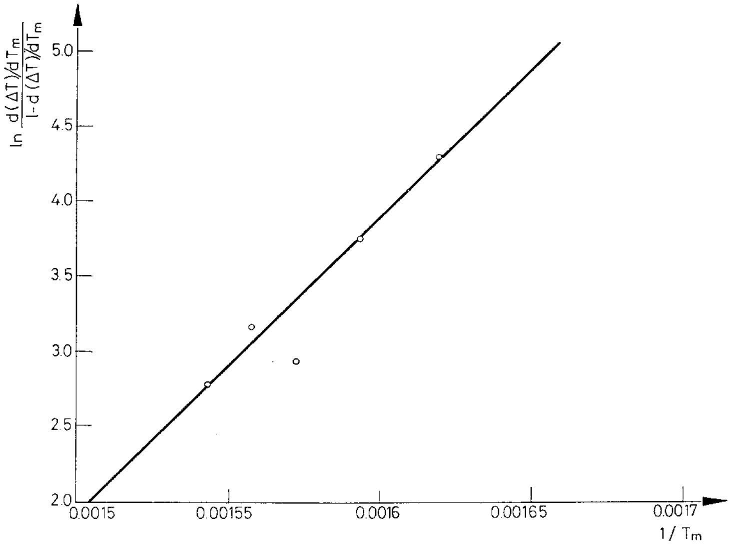

Fig. 5. Plot for the determination of the energy of activation

If it is assumed now that C is constant over a very small range of the process when the reaction starts:

$$\ln C - \frac{E}{RT_M} = \ln \frac{d(\Delta T)/dT_M}{1 - \dfrac{d(\Delta T)}{dT_M}} \tag{11}$$

where $\ln \dfrac{d(\Delta T)/dT_M}{1 - \dfrac{d(\Delta T)}{dT_M}}$ is a linear function of $1/T_M$ in the range where C is a constant, being $-E/R$ the slope. The shape of the curve (Fig. 4, curve 5) is such that the slope of ΔT in function of T_M increases with T_M, [① → ②]; over point ② the slope decreases with T_M, [② → ③]. The range [① → ②] is the only region where our assumptions are valid; over point ②, C is no longer a constant.

Table 1

Data for the thermal oligomerization of ethylene

T_M, K	ΔT_M, K	$\ln \dfrac{d(\Delta T)/T_M}{1 - d(\Delta T)/dT_M}$	$1/T_M$,K^{-1}
613	0.08	—	—
617.5	—	−4.304	0.001619
622	0.2	—	—
627.5	—	−3.7612	0.001593
633	0.45	—	—
636	—	−2.944	0.001572
639	0.75	—	—
642	—	−3.1655	0.001557
645	1.0	—	—
648	—	−2.780	0.001543
651	1.35	—	—

1. A — Frequency factor in the Arrhenius' equation.
2. c_v — Heat capacity at constant volume.
3. ΔH_r — Heat of reaction per reacted mole.
4. ΔT — Temperature difference of sample and reference.
5. E — Activation energy.
6. F — Factor that involves the partial pressures of the reaction components (influence of concentration upon rate of reaction).
7. q — Heat generated per unit time.
8. θ — Time.
9. r — Reaction rate.
10. R — Universal gas constant.
11. T — Temperature.
12. T_M — Temperature of sample.
13. T_R — Temperature of reference.

The value obtained from the above data for the activation energy of ethylene was: 34.7 kcal/mole, that is in good agreement with the reported value.

Experimental, results and discussion

The DTA curves for the oligomerization of ethylene, with or without catalyst were obtained (Fig. 4, curves 1, 2, 3, 4, 5). This shows clearly the difference in the initiation temperature which is very favorable for those catalysts made of 15% Ni or Co on activated charcoal.

The analysis of the products by mass spectrometry and gas chromatography showed a high per cent of olefins between C_6 and C_{12}. The curve for the thermal reaction without catalyst was selected to calculate E.

It is important to note that the thermal reaction (Fig. 4, curve 5) can be divided for its analysis. In the region to the left of point ① the reaction has not started. The region between points ① and ② corresponds to the initiation of the thermal reaction; in this region the assumption of C = constant is valid and Eq. (11) applies to the behavior in that part. In the range between points ② and ③, C is obviously not a constant.

In fact, the slope of the curve (region [① → ②]) increases with temperature T_M, which agrees with Eq. (11), where $\dfrac{d(\Delta T)/dT_M}{1 - \dfrac{d(\Delta T)}{dT_M}}$ must be positive. In the region ② → ③, the slope of the curve decreases with T_M, which is implied by Eq. (11) where C is assumed constant.

The region between points ③ and ④ corresponds to energy dissipation due to the heat of reaction when the reaction has finished.

Eq. (11) permits us to calculate E from the experimental data for region [① → ②]

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Résumé — On présente les considérations théoriques et les données expérimentales utilisées pour calculer l'énergie d'activation de l'oligomérisation de l'éthylène en utilisant un micro-réacteur dans un appareil ATD.

Zusammenfassung — Die theoretischen Erwägungen und die Versuchsangaben zur Berechnung der Aktivierungsenergie der Äthylen-Oligomerisierung unter Anwendung eines Mikroreaktors in einem DTA-Gerät werden angeführt.

Резюме — Представлены теоретические соображения и экспериментальные данные по расчету энергии активации процесса образования олигомеров этилена при использовании микрореактора в приборе для дифференциального термического анализа.