Note Phenomenology and Kinetics of the Reaction Between Sulfur and Atactic Polypropylene

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NOTE
PHENOMENOLOGY AND KINETICS OF THE REACTION
BETWEEN SULFUR AND ATACTIC POLYPROPYLENE

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INTRODUCTION

While sulfur has been widely used as a dehydrogenating agent, in particular to obtain conjugated dienes [1-4], there is no kinetic information available about its effect on atactic polypropylene (APP), only Dontsov et al. [5] mentioning the products of this reaction, while Stefanovskaya et al. [6] studied the kinetics of the rather similar reaction with tetrachloro-o-benzoquinone. Also worth mentioning are the kinetic studies carried out by Dontsov et al. [7-11] on the reaction kinetics of polyethylene with sulfur, unsaturation, crosslinks, and mercaptides being the main products and the processes being first-order with activation energies of approximately 120 kJ/mol.

When a mixture of sulfur and APP is heated in N_2, no carbon disulfide, mercaptides, or thiophene (all possible by-products according to references) are formed, but a significant amount of H_2S evolves. The IR spectra of treated APP (see Fig. 1) show absorption bands attributable to a $R_1 R_2 C{=}CHR_3$ double bond. When the process is carried out above 170°C and for more than 8×10^4 s, a peak attributable to a C=S group appears. Hence, it was decided to study the dehydrogenation kinetics in bulk by measuring the H_2S evolved at 120-170°C (so that only C=C groups are formed) in the absence of catalysts.
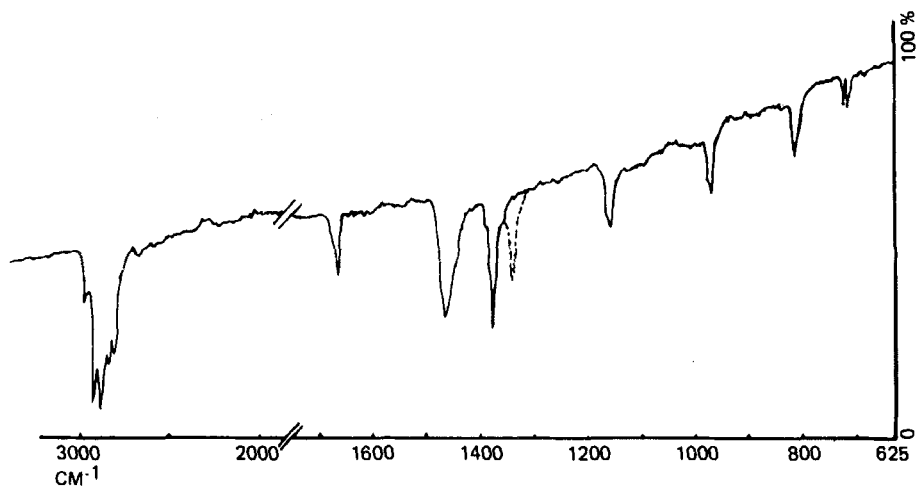
FIG. 1. Infrared spectrum of a sample of APP after heating at 150°C with sulfur for 3 h. The dotted line indicates the additional peak which appears when the same experiment is carried out at 170°C or above.

EXPERIMENTAL

The H_2S formed in the reactor (see Fig. 2) is carried by a N_2 stream into a conductance cell containing aqueous 0.1 M KOH. The variation in conductance was converted into kinetic data by using a calibration curve obtained by measuring KOH samples containing known amounts of H_2S.

The APP used was TAQSA "U" quality, $\bar{M}_n$ 8000, purified by steam current distillation and washing to remove catalyst residues, followed by heating at 170°C and 40 torr. Sulfur and KOH were ERBA reagent grade. Water was Milli-Q grade.

RESULTS AND DISCUSSION

The overall reaction is first order with respect to both sulfur and APP (see Fig. 3), while the overall order is two, and has an activation energy of 63.7 kJ/mol (about half that found for polyethylene) and an Arrhenius preexponential factor of 67.5 m^3/(mol·s) (so low that activation must be intermolecu-
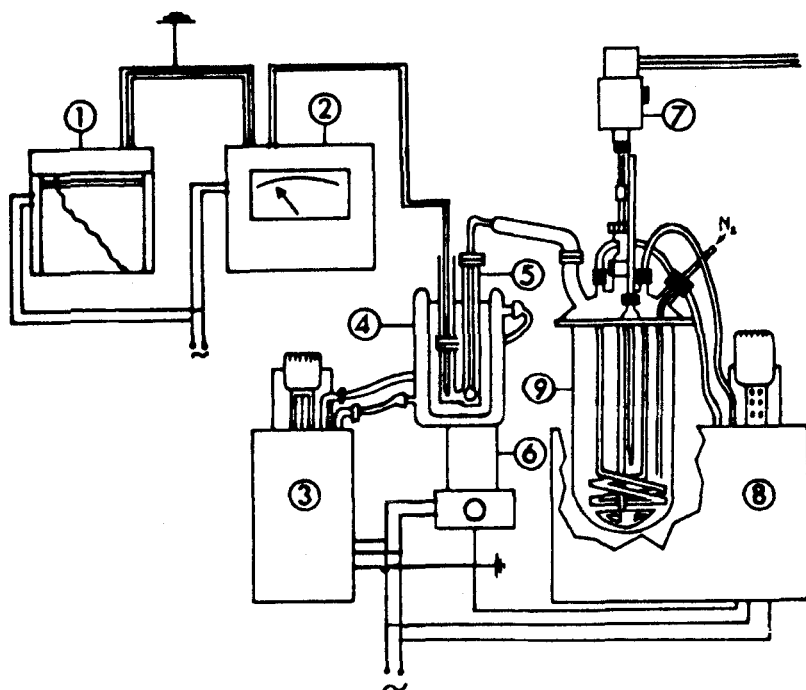
FIG. 2. Experimental apparatus: (1) Recorder, (2) conductance meter, (3) cell thermostat, (4) thermostated conductance cell, (5) Gas disperser, (6) cell stirrer, (7) reactor stirrer, (8) oil bath, (9) reactor with internal heating coil.

lar). The low activation entropy, 1.56 kJ/mol, indicates that activation takes place on the chain, which remains largely unaltered by transition state formation. References 7-11 consider that the reaction takes place via the formation of a C—SH group which later decomposes. From our experimental data, and taking into account the structure of liquid sulfur, the reaction sequence should be as follows:

$$S_8 \rightleftharpoons \cdot S_8 \cdot \qquad (1)$$

$$-CH_2-CH(CH_3)- + \cdot S_8 \cdot \longrightarrow -CH_2-C(CH_3)SH-, \quad \Delta H^\circ = -208 \text{ kJ/mol} \qquad (2)$$
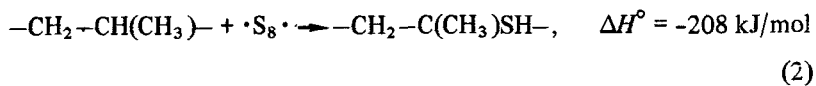
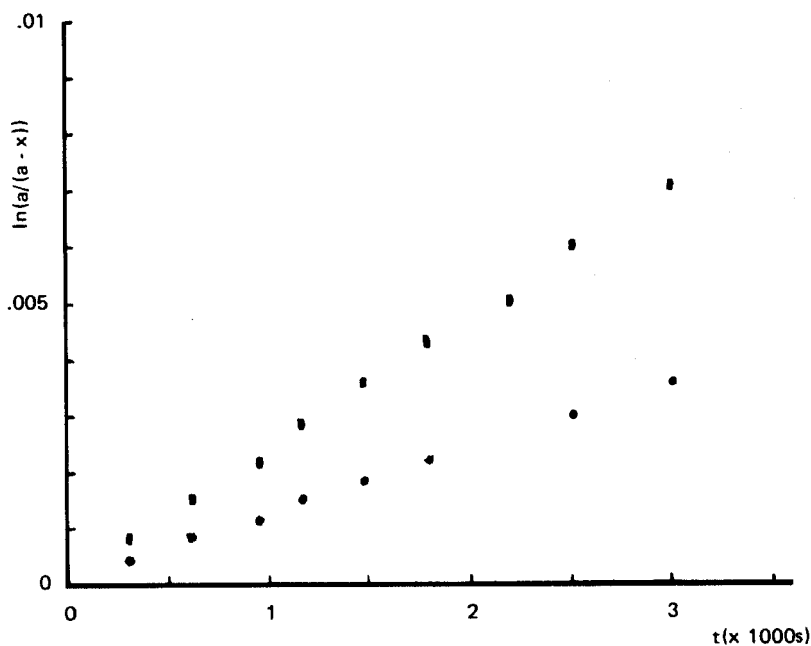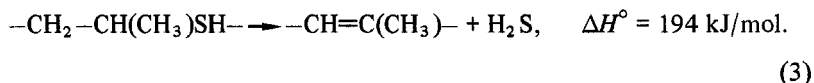FIG. 3. Plots for ln $(a/a - x)$ vs t for the reaction between APP and S when carried out with an excess of S at 393 K (upper) and with an excess of APP at 453 K (lower).

$$-CH_2-CH(CH_3)SH-\longrightarrow-CH=C(CH_3)-+H_2S, \quad \Delta H° = 194 \text{ kJ/mol.}$$

(3)

This sequence can also explain C=S formation via

$$-CH_2-C(CH_3)SH-\longrightarrow-CH_2-C(CH_3)S\overset{\bullet}{-}-\longrightarrow-CH_2-CS-+CH_4, \quad (4)$$

the reaction enthalpies (calculated using Ref. 12) seem to contradict it, since it seems logical to assume that Reaction (2) is the rate-determining step, being strongly endothermal, and the overall order in this case ought to be one instead of two. Yet there is a justification: Using an Arrhenius factor of 10×10^5 m^3/(mol·s) (normal for gas-phase bimolecular reactions with nonlinear transition state [13]) and the experimental activation energy, the rate constant of Reaction (2) in the gas phase can be determined and, from it the

TABLE 1. Rate Constants for the Reaction between APP and S at 166°C

	Gas phase	Condensed phase
Experimental, $m^3/(mol \cdot s)$	—	1.79×10^{-6}
Thiol formation (calculated), $m^3/(mol \cdot s)$	2.65×10^{-3}	3.34×10^{-3}
Thiol decomposition (calculated), s^{-1}	6.81×10^{11}	6.81×10^{11}

corresponding condensed-phase one [14] (assuming vaporization enthalpies for APP and for the thiol to be nearly identical). Reaction (3) in the gas phase will have a factor of 1×10^{12} to 1×10^{14} $m^3/(mol \cdot s)$ [13] and, considering its activation energy to be similar to the reaction enthalpy (potential barrier height is negligible for strong endothermal reactions), the rate constant for Reaction (3) in the condensed phase can be obtained (Table 1). It can be seen the Reaction (3) is much faster than Reaction (2), and the calculated value of k_2 (considering the approximations made) is not unlike the experimental one. It can then be assumed that the proposed reaction sequence is plausible.

REFERENCES

[1] F. Asinger, M. Thiel, and R. Sowada, *Monatsh. Chem.*, *90*, 402 (1959).
[2] H. Wynberg, *J. Am. Chem. Soc.*, *80*, 364 (1958).
[3] M. Thiel, F. Asinger, and K. Schmiedel, *An. Chem. A*, 611,121.
[4] H. Juraszyk, *Chem. Ztg.*, *98*, 126 (1974).
[5] A. Dontsov, F. Farka, G. Ermilova, and B. Dogadkin, *Plast. Massy*, p. 28 (1965); *Chem. Abstr.*, *64*, 5255.
[6] N. Stefanovskaya, I. Favrilenko, and I. Markevicht, *Izv. Akad. Nauk SSSR, Ser. Khim.*, p. 2355 (1967).
[7] A. Dontsov and B. Dogadkin, *Vysokomol. Soedin.*, *3*, 1746 (1964).
[8] A. Dontsov and B. Dogadkin, *Ibid.*, *6*(10), 1744 (1964).
[9] A. Dontsov and B. Dogadkin, *Ibid.*, *6*(10), 1748 (1964).
[10] A. Dontsov and B. Dogadkin, *Ibid.*, *6*(11), 2015 (1964).
[11] A. Dontsov and B. Dogadkin, *Ibid.*, *6*(11), 2023 (1964).
[12] *Handbook of Chemistry and Physics*, 57th ed., CRC Press, 1967, pp. F219-240.

[13] F. Wilkinson, *Chemical Kinetics and Reaction Mechanisms,* Van Nostrand
       and Reinhold, New York, 1980, p. 124.
[14] Ref. 13, p. 141.

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