CHEMISTRY

1961

SovietRxiv

Fig. 1. Effect of temperature on the kinetics of ammonia formation during decomposition of DPG. 1 –136°, 2 –145°, 3 –157°, 4 –170°, 5 –180°.

Figure 1: Fig. 1. Effect of temperature on the kinetics of ammonia formation during decomposition of DPG. 1 –136°, 2 –145°, 3 –157°, 4 –170°, 5 –180°.

Abstract

Full Text

CHEMISTRY

B. A. DOGADKIN and N. N. PAVLOV

THERMAL DECOMPOSITION OF DIPHENYLGUANIDINE AND ITS INTERACTION WITH SULFUR AT VULCANIZATION TEMPERATURE

(Presented by Academician A. A. Balandin, 28 I 1961)

Diphenylguanidine (DPG) is one of the most widely used vulcanization accelerators, ensuring high dynamic properties of vulcanizates. Meanwhile, the mechanism of action of DPG has not yet been elucidated. In this connection, it was of interest to consider the process of thermal decomposition of DPG under the temperature conditions of vulcanization and to investigate its reaction with sulfur.

Decomposition of DPG in the melt. When DPG is heated at 140° in an argon atmosphere, as was established earlier (1), ammonia is evolved and aniline, tetraphenylmelamine, and small amounts of triphenyldicarbamide are formed. The evolution of ammonia becomes noticeable at 136°, i.e., at the vulcanization temperature (Fig. 1).

Fig. 1. Effect of temperature on the kinetics of ammonia formation during decomposition of DPG. 1 –136°, 2 –145°, 3 –157°, 4 –170°, 5 –180°.

At 136 and 145° the formation of ammonia proceeds at a constant rate; in the temperature interval 157–180° the process is described by the equation for a first-order reaction. The apparent activation energy of the ammonia-formation process for the indicated three temperatures is 25.7 kcal. The experimental data show that in 30 min at 140° approximately 50% of the accelerator taken decomposes. In a study of the vulcanization of natural rubber it was established (2) that the loss of DPG by 30 min of vulcanization amounted to 40%, and by 90 min to about 50%; moreover, the presence of zinc oxide in the system has a substantial effect on the rate of DPG consumption.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

Decomposition of DPG in solution. High-boiling hydrocarbons with different dipole moments were chosen as solvents.

(naphthalene 0, xylene 0.62, isopropylbenzene 0.65, glycerol 2.96). The decomposition was carried out at 140° in a stream of argon for 5-6 h. As is seen from Fig. 2, the character of the kinetic curves for ammonia formation during decomposition of the accelerator in solution and in the melt is analogous. No substantial effect of the solvents on the rate of ammonia formation (as a function of the dipole moment) was found in the initial stage of the reaction. The latter may serve as indirect evidence for the possibility that decomposition proceeds by a homolytic mechanism. Decomposition of DPG in a xylene solution of rubber makes it possible to conclude that there is no interaction of DPG and intermediate products of its decomposition with polymer molecules. The amount of ammonia formed in this case agrees sufficiently well with the data obtained on decomposition of the accelerator in pure xylene (Fig. 2). According to viscosity measurements, prolonged heating of rubber solutions at 140° together with DPG likewise does not cause any noticeable structural changes in the polymer.

Fig. 2. Effect of solvents on the kinetics of ammonia formation at 140°. 1 –*o*-xylene, 2 –isopropylbenzene, 3 –naphthalene, 4 –glycerol, 5 –solution of rubber in *o*-xylene

Interaction of DPG with sulfur. The reaction was carried out in *o*-xylene, with the accelerator-sulfur ratio varied from 1 : 0.25 to 1 : 4. The reaction is accompanied by the formation of resin-like nonvolatile products and by the evolution of hydrogen sulfide. The process proceeds at a constant rate only in the case of a molar accelerator-sulfur ratio (Fig. 3, 1). Decreasing the concentration of added sulfur to 0.25-0.5 mole per 1 mole of accelerator leads to the appearance of an induction period (curves 2 and 4). Increasing the sulfur concentration to 4 moles per 1 mole of DPG substantially changes the shape of the kinetic curve for hydrogen sulfide formation (curve 3). The presence of an induction period on the kinetic curves for hydrogen sulfide formation can apparently be associated with the formation of salt complexes of the type $C_{13}H_{13}N_3 \cdot H_2S$, since in the initial stage of the reaction the system contains an excess of undecomposed DPG. With an increase in the sulfur concentration, the equilibrium of the reaction of formation and decomposition of the salt-like

Fig. 3. Effect of the DPG : S ratio on the kinetics of formation of H_2S in *o*-xylene at 140°. 1 –1:1, 2 –2:1, 3 –1:4, 4 –1:0.25.

Fig. 4. Ultraviolet absorption spectra of the products of the reaction of DPG with sulfur at 140°. The curve numbers correspond to fractions obtained in chromatographic separation of the mixture.

Figure 4: Fig. 4. Ultraviolet absorption spectra of the products of the reaction of DPG with sulfur at 140°. The curve numbers correspond to fractions obtained in chromatographic separation of the mixture.

of the complex shifts toward the evolution of large amounts of free hydrogen sulfide. Data characterizing the yield of hydrogen sulfide in equivalents of the sulfur introduced are given below:

DPG : sulfur ratio, mol	Fraction of sulfur as H_2S, relative to initial
1 : 0.25	0.00295
1 : 0.5	0.00209
1 : 1.0	0.00137
1 : 4.0	0.0007

From these data it follows that 2 mol of DPG are consumed in the formation of 1 mol of hydrogen sulfide.

The nonvolatile reaction products were separated by chromatography of the mixture on aluminum oxide. Individual fractions of the isolated crystalline and resin-like products, after appropriate purification, were examined spectrally in the infrared and ultraviolet regions of the spectrum.

Fig. 4. Ultraviolet absorption spectra of the products of the reaction of DPG with sulfur at 140°. The curve numbers correspond to fractions obtained in chromatographic separation of the mixture.

A detailed interpretation of the spectra obtained in the infrared region is complicated by the lack of sufficiently reliable data on the positions of absorption bands for aromatic amines and their derivatives. In addition, interpretation of the characteristic bands for the N—H bond in secondary aromatic amines is difficult, since in this region there are absorption bands due to valence vibrations of the C=C bond in the ring. Consideration of the absorption spectra in the UV region makes it possible to conclude that sulfur-containing groupings are present in the compounds studied. The character of the spectral curves in this region of the spectrum is analogous to spectral curves obtained by various authors in the study of low-molecular linear sulfides (Fig. 4). The presence of fairly distinct absorption maxima in the 300-380 mμ region may be attributed to the presence in the mixture under study of linear polysulfides containing from 2 to 5 sulfur atoms. The presence of an absorption band in the IR spectrum at 1480-1490 cm^{-1} and at 590-620 mμ in the UV spectrum may be attributed to the C=S group. Absorption at 1335-1355 cm^{-1} is apparently due to the presence of $C_6H_5NH_2$. The presence of absorption at 1480–1490 cm^{-1} and 590–620 mμ, correspond-

containing a thioketo group, gives grounds for assuming that, along with the process of decomposition of the accelerator and the formation of polysulfides, there occurs a process of interaction of H_2S with the accelerator molecule, leading to the formation of a thiourea derivative. The formation of the indicated product can evidently be represented by analogy with the interaction of guanidine and its derivatives with water.

Moscow Institute of Fine
Chemical Technology
named after M. V. Lomonosov

Received
26 I 1961

REFERENCES

1. Rathke, Oppenheim, Ber., **23**, 1672 (1890).
2. Wistinghausen, Kautschuk, **5**, 57, 75 (1929).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.