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THE PSEUDOBINARY PHASE DIAGRAM CIS-/TRANS-AZOBENZENE AND THE CIS ⟶ TRANS ISOMERIZATION IN VARIOUS STATES OF AGGREGATION

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Azobenzene, Phase Diagram cis-/trans-azobenzene, Kinetics of Isomerization

The pseudobinary phase diagram of trans-azobenzene and the thermally instable cis-isomer was examined by thermomicroscopical and DSC-measurements. Two eutectic temperatures have been determined (at 41.4 °C and 36.7 °C). The latter occurs only in the presence of a metastable polymorph of cis-azobenzene after quenching a melt, that contained as well cis- as trans-azobenzene, presumable under conditions of heterogeneous nucleation. In the melt and in solution the thermally induced cis-trans-isomerization follows first order kinetics. Below the eutectic temperature the rate is controlled by three-dimensional nuclei growth to reaction extent 0.20. Between the eutectic temperature and the melting points of product respectively educt the kinetics follow the PROUT-TOMPKINS law. The reason is the increasing isomerization rate with increasing fraction of melt.

Introduction

Investigation of the kinetics of the thermal cis → trans-isomerization of azobenzene (Fig. 1) in the solid state imply knowledge of the melting diagram. If a pure solid state reaction shall be examined - without any participation of melt - one must be sure that the temperature range is below the eutectic temperature of educt and product. Because of the thermal instability of the cis-isomer the system cis-/trans-azobenzene must be characterized as a pseudobinary system, since one compound (trans) is the isomerization product of the other (cis). To determine the phase diagram we have undertaken thermomicroscopical and DSC-measurements.

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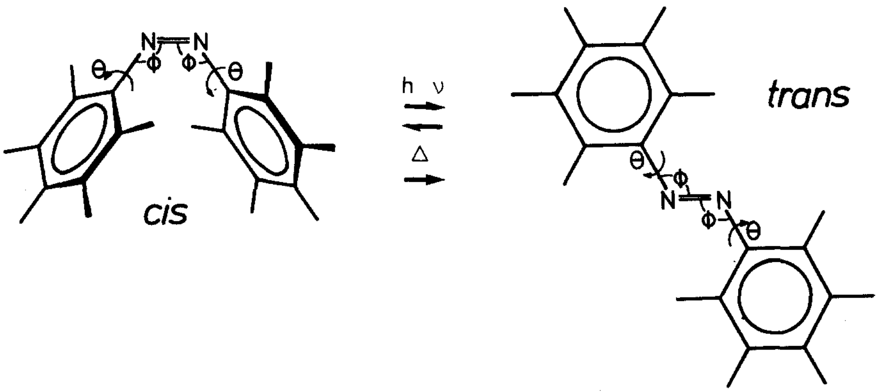


Fig. 1 Structure and conformation of cis- and trans-azobenzene. Ø Valence angle, θ torsion angle. Trans-azobenzene: $Ø \approx 114^{o}$, $\theta \approx 15^{o}$ [1]; cis-azobenzene: $Ø \approx 121^{o}$, $\theta \approx 53^{o}$ [2]

Determination of the Phase Diagram

The eutectic temperature can be estimated by KOFLER's "contact preparation method" [3]. Pure, finely powdered cis- and trans- azobenzene were placed side by side in a glass crucible with a slide cover glass (Mettler FP 84). The sample was rapidly heated until melting, cooled and then the material allowed to solidify. By heating a second time, melting occurs at first by reaching the eutectic temperature in that region of the sample, where the mixing zone contains the eutectic composition. In this way the eutectic temperature was determined in 6 independent measurements (41.9±0.1 ^{o}C). The eutectic composition was estimated from measurements with weighed mixtures containing different portions of cis- and trans-azobenzene (eutectic composition: $X_{trans} = 0.52$).

Additional DSC-measurements (Heraeus TA 500) were carried out with pure cis-azobenzene as starting material. Heating up the sample, the endothermic melting peak ($\vartheta_{fus} = 71.6$ ^{o}C) passes over directly into the exothermic isomerization peak (Fig. 2).

Quenching the sample after complete melting (80 ^{o}C) and taking up a new DSC-measurement, the sample now contains a certain amount of trans-azobenzene. The eutectic melting peak becomes visible. Starting with pure cis-azobenzene it is in principle possible to determine the whole phase diagram with only one single sample, because the composition is shifted towards higher content in trans-azobenzene after each DSC-run.

If the melting enthalpies of both substances and the eutectic composition are known, the composition of the sample can be determined from the ratio of the peak areas. The eutectic temperature can be estimed from the onset-temperature of the eutectic peak and the melting temperature of the excess material from the maximum of the melting peak.

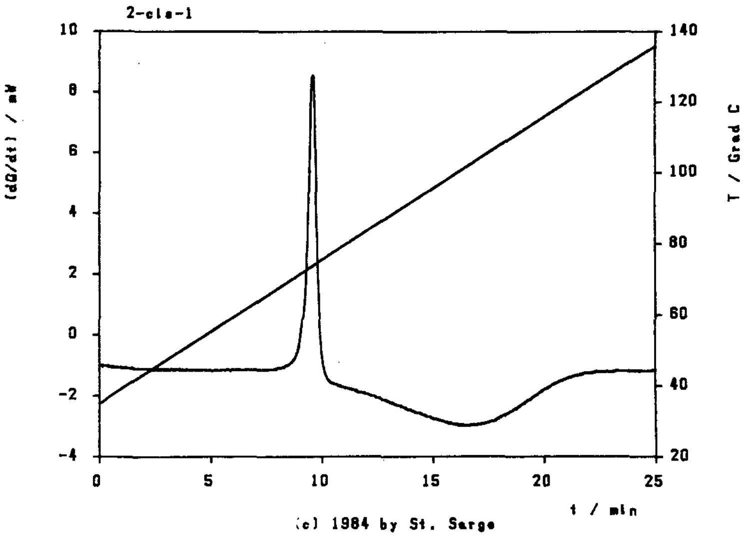


Fig. 2 DSC-trace for melting (endothermic peak) and isomerization (exothermic peak) of cis-azobenzene

For the evaluation of the DSC-curves the melting enthalpy of cis-azobenzene was taken equal to that of trans-azobenzene (trans-azobenzene: ΔH_{fus} = 22.65 kJ mol^{-1} [4], cis-azobenzene: ΔH_{fus} = 21.8 kJ mol^{-1} [5] respectively 21.5 kJ mol^{-1} [6]), what leads to a maximum error of +0.5 % with regard to X_{trans}.

During the measurements it became apparent, however, that two eutectic temperatures exist: ϑ_{eu1} = 41.4 °C and ϑ_{eu2} = 36.7 °C. The first eutectic temperature is in good accord with the data of the thermooptical analysis. When the lower melting eutectic occured, also the melting points of cis-azobenzene (liquidus line) were lowered compared with the other melting curve. Fig. 3 shows two DSC-traces with the same extent and the same treatment of the samples. The sample with the higher melting points had been quenched in liquid nitrogen, the other in icy water in an ultrasonic bath. The shift of the melting peaks (with the same composition) is clearly recognizable.

The lower melting eutectic occured only after quenching a melt that contained as well cis- as trans-azobenzene. It was impossible to produce it at will by different methods of supercooling (icy water or liquid nitrogen). Mixtures that had not been melted always showed the higher melting eutectic. The lower melting eutectic could be observed by thermooptical analysis just when the melt solidified instantly after taking the glass crucible out of the Mettler FP 84. The reason for this could be heterogeneous nucleation. Generally, the melt of cis-azobenzene can be supercooled very far.

Possibly, cis-azobenzene under the conditions of heterogeneous nucleation shows a second modification forming a second eutectic with trans-azobenzene. All attempts to produce greater amounts of this modification to clarify this question by X-ray diffraction were hitherto not successful.

Fig. 4 shows the results of our measurements in a phase diagram and in addition the values of GALASHIN et al. [7]. These authors determined a eutectic temperature of 40 °C and a eutectic composition of X_{trans} = 0.40. Especially in the region between 40 % and 60 % trans-azobenzene they estimated considerably higher melting points, what naturally leads to another eutectic composition. About their preparation of the samples and their methods of measurement they do not tell any details, except for the fact that they investigated physical mixtures and not solidified melts. So it is not astonishing that they observed no second eutectic.

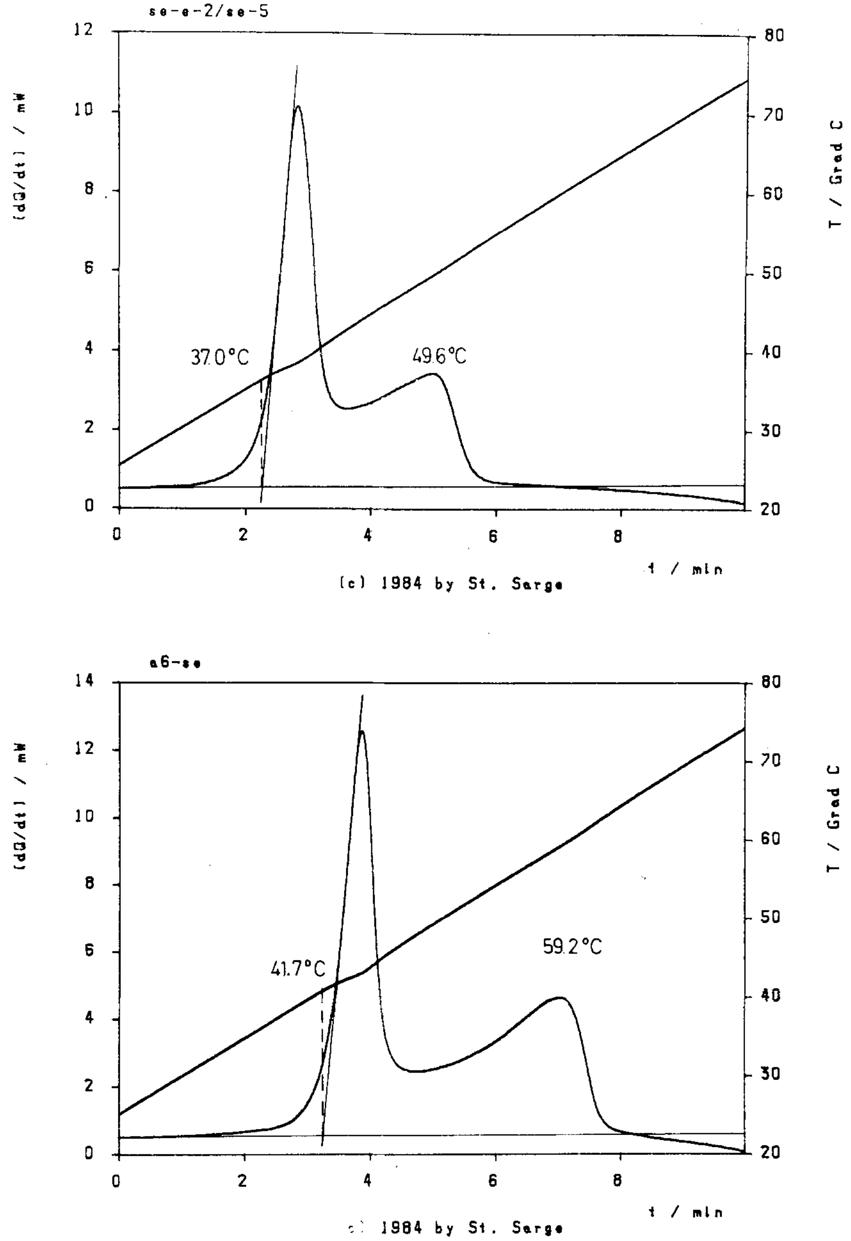


Fig. 3 Two DSC-measurements with X_{trans} = 0.27; melt quenched in icy water in an ultrasonic bath (above) and in liquid nitrogen (below).

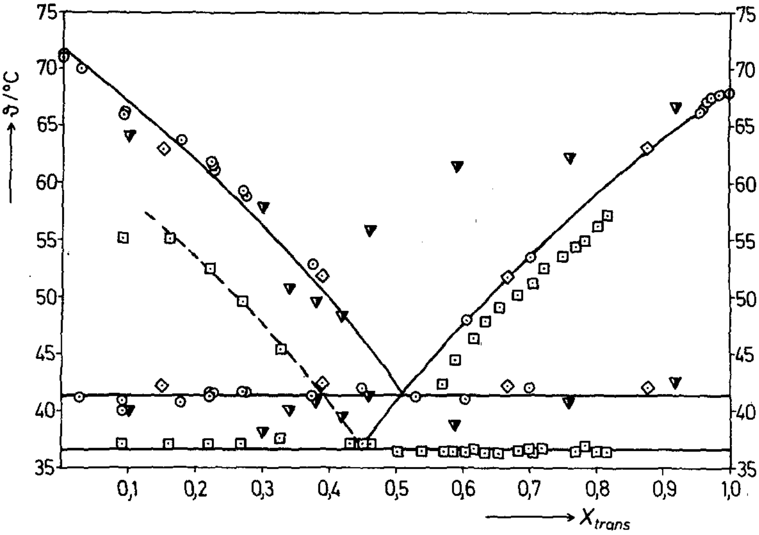


Fig. 4 Pseudobinary melting diagram of the system cis-/trans-azobenzene. ⊙ , ⊡ DSC measurements with quenched, solidified melts, ◇ DSC-measurements with physical mixtures, ▼ data of GALASHIN et al. [7]

The Isomerization of cis-Azobenzene in Various States of Aggregation

We examined the kinetics of the thermally induced cis ⟶ trans-isomerization of azobenzene in solution, in the melt, and in the crystalline state below and above the eutectic temperature. Fig. 5 summarizes the $\alpha(t)$-curves on a reduced time scale. In the vapour phase [8], the melt, and in solution (n-hexane) the isomerization follows first order reaction kinetics. Starting the reaction with crystalline material the $\alpha(t)$-curves show a sigmoidal shape.

The isomerization reaction in the melt can be followed by discontinuous sampling or by DSC measurements. Since pure cis-azobenzene as starting material can be easily supercooled, the isomerization kinetics in the melt can be determined in the temperature range from 10 °C to 120°C by DSC, see Fig. 6.

The evaluation was done according to the method of BORCHARDT and DANIELS [5].

Below the eutectic temperature the solid state reaction can be described by two overlaying regions: the first region ($\alpha < 0.2$) is characterized by three-dimensional nuclei growth, in the second region ($\alpha > 0.2$), the reaction kinetics can be mathematically described by a three-dimensional diffusion law [9].

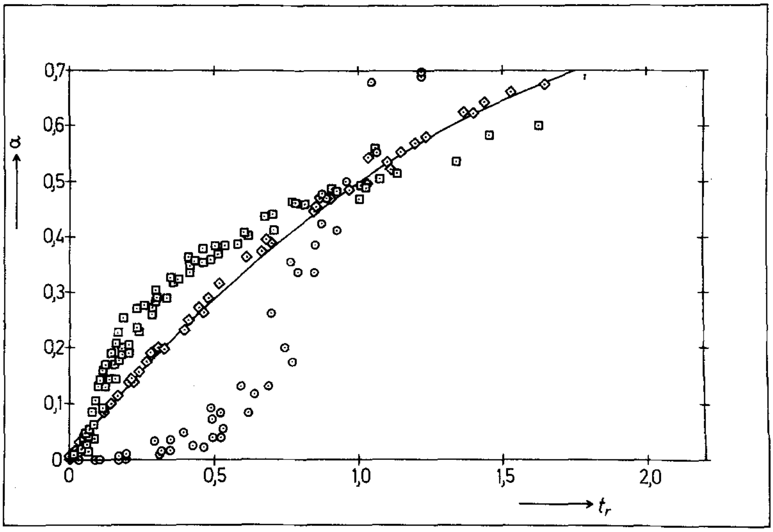
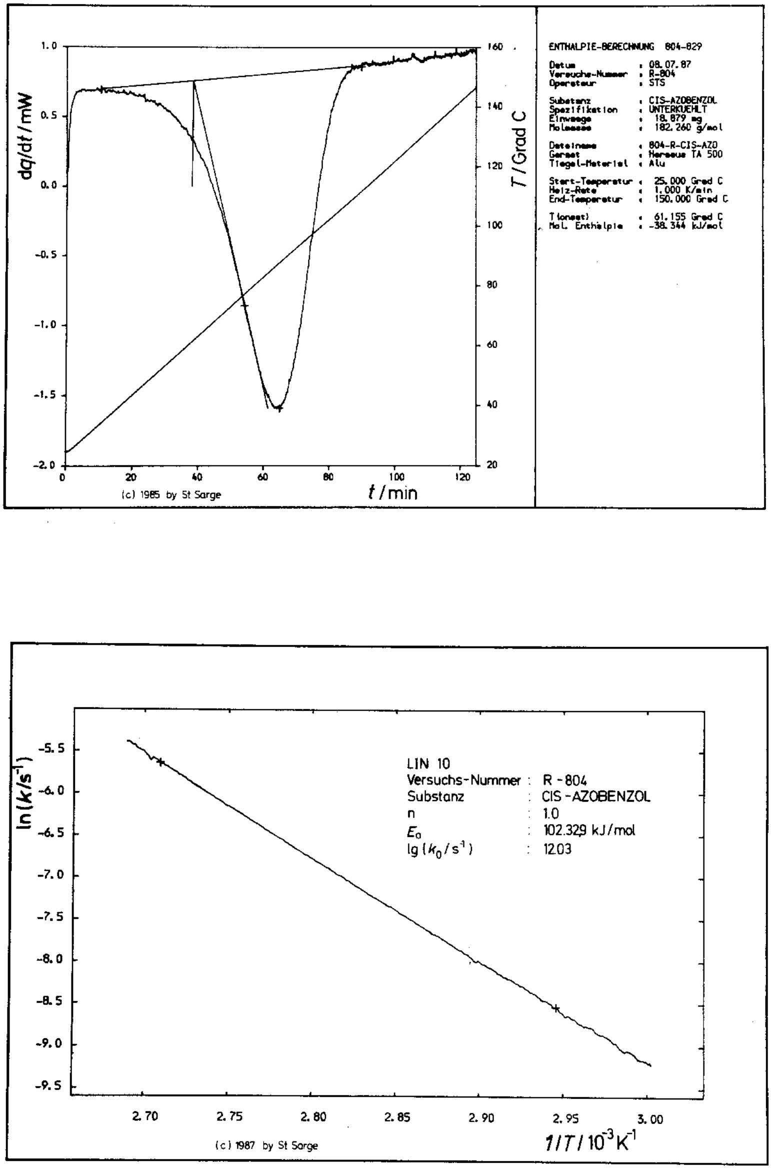


Fig. 5 cis → trans isomerization in various states of aggregation: —— melt; ◇ n-hexane; solid state reaction below ⊙ and above ⊡ eutectic temperature; fraction reacted versus reduced time $t_r = t/t_{0.5}$.

Above the eutectic temperature up to $\alpha \approx 0.5$ the kinetics follow the PROUT-TOMPKINS law (branching nuclei) [5]. The acceleration of the reaction certainly cannot be referred to branching of solid nuclei. As we have shown by thermooptical analysis the reason is the increasing isomerization rate with increasing fraction of melt. At higher extent than the eutectic composition only isomerization in the melt occurs with a first order kinetic law.



ENTHALPIE-BERECHNUNG 804-829

Datum : 08.07.87
Versuchs-Nummer : R-804
Operateur : STS

Substanz : CIS-AZOBENZOL
Spezifikation : UNTERKUEHLT
Einwaage : 18.879 mg
Molmasse : 182.260 g/mol

Dateiname : 804-R-CIS-AZO
Geraet : Heraeus TA 500
Tiegel-Material : Alu

Start-Temperatur : 25.000 Grad C
Heiz-Rate : 1.000 K/min
End-Temperatur : 150.000 Grad C

T(onset) : 61.155 Grad C
Mol. Enthalpie : -38.344 kJ/mol

LIN 10
Versuchs-Nummer : R-804
Substanz : CIS-AZOBENZOL
n : 1.0
E_a : 102.329 kJ/mol
lg(k_0/s^{-1}) : 12.03

Fig. 6 Isomerization of cis-azobenzene in a supercooled melt. Exothermic isomerization peak (above) and the resulting ARRHENIUS-plot.

In Table 1 the activation enthalpies calculated for a temperature of 333 K are summarized:

Table 1 Activation enthalpies of the cis → trans isomerization of azobenzene in all states of aggregation

	$\Delta H^{\neq}_{333}$	$\Delta G^{\neq}_{333}$	Lit.
	kJ mol^{-1}		
Vapour	115	111	[8]
n-hexane solution	85.1	107.4	[*]
melt, isothermal, discont. sampling	100.6	107.4	[5]
melt, dyn., evaluation by method of BORCHARDT and DANIELS	100.8	108.6	[5]
melt, supercooled; DSC, evaluation by method of BORCHARDT and DANIELS	100.5	107.6	[*]
crystal above ϑ_{eu1}	220	107	[5]
crystal below ϑ_{eu1}			
accleratory regime	129	110	[*]
deceleratory regime	173	116	[*]

* This work

Fig. 7 shows the $\alpha(t)$-curves at two different temperatures. To provide random nucleation the reaction behaviour in quenched solid samples with as close as possible to eutectic composition was investigated. At temperatures above the metastable eutectic ϑ_{eu2} melting occurs in many quenched samples, if these contained the metastable eutectic. These samples then show the same rate as calculated for a completely molten sample for the same temperature.

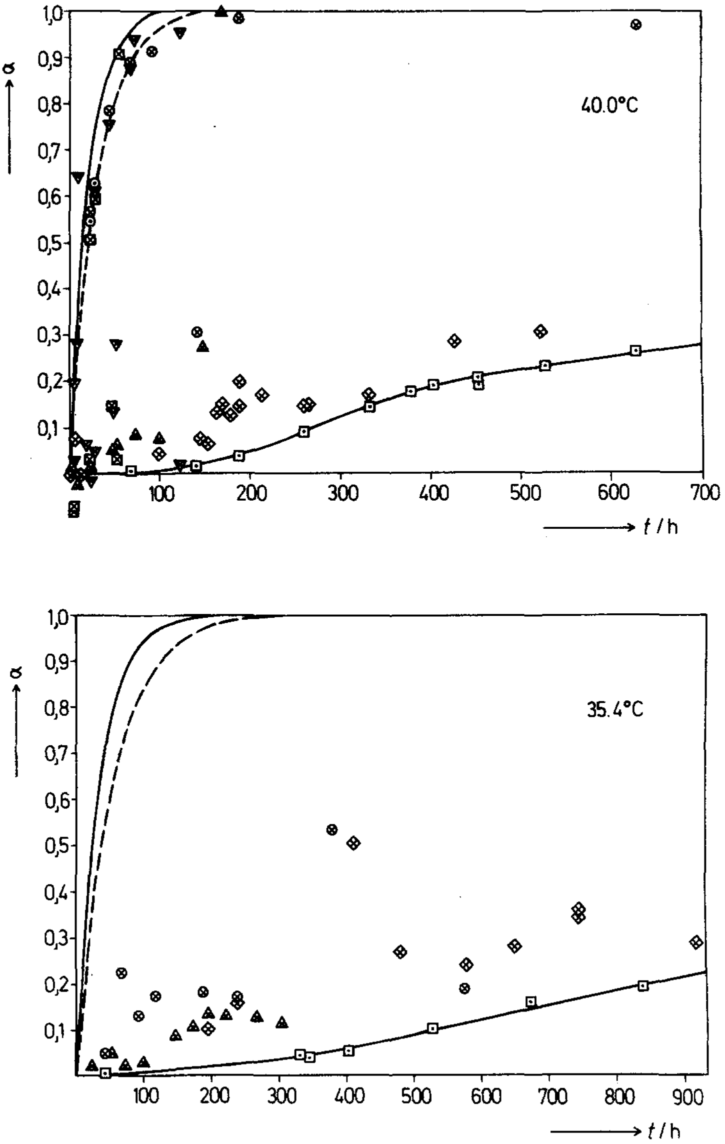


Fig. 7 Conversion versus time for the thermal isomerization at 35.4 °C resp. 40.0 °C. ⊡ Starting with crystals of pure cis-azobenzene; —— isomerization in n-hexane; – – – isomerization in the melt. All other symbols represent isomerization of quenched, solidified melts (α = 0.52 as starting composition).

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Zusammenfassung - Das pseudobinäre Phasendiagramm von trans-Azobenzol und des thermisch instabilen cis-Isomeren wurde mit Hilfe thermomikroskopischer und DSC-Messungen untersucht. Es wurden zwei Eutektika bestimmt /bei 41.4 °C und 36.7 °C/, wobei das zweite Eutektikum nur in Anwesenheit einer metastabilen Modifikation von cis-Azobenzol nach Abschrecken einer Schmelze, die gleichzeitig cis- und trans-Azobenzol enthielt, vermutlich bei heterogener Keimbildung entstand. In der Schmelze und in Lösung verläuft die thermische cis-trans-Isomerisierung nach einem Geschwindigkeitsgesetz erster Ordnung. Unterhalb der eutektischen Temperatur ist die Festkörperreaktion bis zu Umsätzen von 0,20 durch dreidimensionales Keimwachstum bestimmt. Zwischen eutektischer Temperatur und Schmelzpunkt lässt sich die Reaktion durch die Gleichung von PROUT-TOMPKINS beschreiben, was auf die zunehmende Isomerisierungsgeschwindigkeit mit zunehmendem Anteil Schmelze zurückzuführen ist.

Резюме - Методом термомикроскопии и ДСК изучена псевдобинарная фазовая диаграмма транс-азобензола и термически нестабильного цис-изомера. Определены две температурные эвтектики при 41,4 и 36,7°. Последняя наблюдается только в присутствии метастабильного полиморфа цис-азобензола после быстрого охлаждения расплава, содержащего как цис-, так и транс-азобензол, и образующегося, вероятно, в условиях гетерогенного образования центров кристаллизации. В расплаве и в растворе термически наведенная цис-транс изомеризация подчиняется реакции первого порядка. Ниже температуры эвтектики скорость реакции контролируется трехразмерным ростом зародышей кристаллов со степенью превращения равной 0,20. В интервале между температурой эвтектики и точками плавления реакция следует кинетике, подчиняющейся закону Праут-Томпкинса. Это является причиной увеличения скорости изомеризации с учеличением доли расплава.