

## Topochemistry. Part 38.<sup>1</sup> Photodimerisation in Mixed Crystals of *trans*-Cinnamamides and of *trans*-Stilbenes

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The phase relations in systems of two cinnamamides and of two *trans*-stilbenes are described. The solid-state photodimerisation of the stilbene system has been investigated, while that of the cinnamamides has previously been reported. The results are consistent with a model in which the reaction takes place in the bulk of crystals composed of random substitutional solid solutions. The model can be refined by considering a slight tendency for like molecules to aggregate in these solutions. There is no evidence for a special role of eutectics. In systems in which a third solid phase of intermediate composition is present the reactivity results can be interpreted by an alternative model.

THIS laboratory has demonstrated<sup>2</sup> the applicability of the topochemical principle to photodimerisation in mixed crystals; the systems studied gave all the possible products of the stereochemistries dictated by the structures of the reacting phases. For a number of acrylic acid and acrylamide pairs the yields of photodimers were determined as functions of starting composition of the two components.<sup>3</sup> These yields were in fair agreement with those calculated on the basis of a model which assumes that the components form random substitutional solid solutions and that there is no transfer of excitation energy from the component which absorbs the radiation to the second component of the system. Contrasting results have been obtained for various substituted anthracenes in which extensive transfer of energy occurs prior to the reaction step.<sup>4,5</sup>

Photoreaction will occur at the site of absorption of light if the rate of reaction there is larger than the rate of transfer of the excitation energy from the site. This is apparently true of the crystalline acrylic acids and amides referred to above, whereas for the anthracenes the converse is true. We considered it of interest to study a system of *trans*-stilbenes, whose energy transfer properties might be intermediate between these two extremes. Such stilbenes can be induced, by dichloro-substitution, to crystallise in structures which allow photodimerisation.<sup>6</sup> We report here the relative yields of photodimers from a reactant system comprising two dichloro-substituted *trans*-stilbenes.

The validity of our conclusion that transfer of energy is not important in the photodimerisations of acrylic acids and acrylamides depends on the validity of the assumption that the pair of reactants forms random substitutional solid solutions over appreciable ranges of composition, the reaction occurring within the bulk of these phases. If, on the other hand, the two components are mutually immiscible then at least the heterodimer would have to be formed at the interface between different crystals, and this would imply prior transfer of energy

from the bulk. Further, for an appreciable yield of heterodimer, the number of monomer molecules at the interface would need to be of the same order of magnitude as the number in the bulk phases, which would be true only for eutectic systems. It is known<sup>7,8</sup> that in some crystal systems reactivity in the eutectic is particularly high in free-radical polymerisation; in the limiting case crystals of the pure components are non-reacting, and polymerisation occurs only when these components form a eutectic. There is no evidence that these polymerisations are topochemically controlled. In the [2 + 2] photodimerisations we are studying, if it appeared that the reaction occurs at interphase surfaces of a eutectic this would disprove our conclusion concerning energy transfer. Further, the fact of topochemical control of such a reaction would provide most intriguing information on the intimate structures of the interphase surfaces.

As a step towards elucidating the site of reaction we investigated, for a pair of cinnamides whose photochemistry we have studied previously and for the pair of dichlorostilbenes, the extent of mutual solid-solubility of the two components. Further, in a search for reactivity specifically at interphase surfaces, we studied the effect of irradiation on a two-component system of which crystals of the pure components are of  $\gamma$ -type structures, *i.e.* are not photoactive.

### EXPERIMENTAL

**Preparations.**—Diethyl 2,4-dichlorobenzylphosphonate was prepared<sup>9</sup> in 80–90% yield by heating  $\alpha$ ,2,4-trichlorotoluene with triethyl phosphite for 16 h. The phosphonate was used directly, without distillation, to give the stilbenes according to the method of Seus and Wilson.<sup>10</sup>

**2,4-Dichloro-3'-methyl-*trans*-stilbene** (1) separated as an oil on treating the phosphonate with toluene-3-carbaldehyde. It was extracted by *n*-hexane, the solution dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent evaporated. Recrystallisation of the residue (MeOH) gave needles, m.p. 54–55°;  $\nu_{\text{max}}$  (KBr) 958 and 965 cm<sup>-1</sup> (*trans*-HC=CH);  $\tau$  (Varian A60; CDCl<sub>3</sub>) 2.3–2.9 (7 H, m, ArH), 2.95 (2 H, s, HC=CH), and 7.6 (3 H, s, CH<sub>3</sub>);

<sup>5</sup> For a review see J. M. Thomas, *Phil. Trans. Roy. Soc.*, 1974, **A277**, 251.

<sup>6</sup> M. D. Cohen, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *Chem. Phys. Letters*, 1970, **7**, 486.

<sup>7</sup> E.g. Gy. Hardy, N. Fedorova, and K. Nyitrai, *European Polymer J.*, 1966, **2**, 349.

<sup>8</sup> E.g. A. Chapiro, *Israel J. Chem.*, 1972, **10**, 129.

<sup>9</sup> G. M. Kosolapoff, 'Organic Phosphorus Compounds,' Wiley, New York, 1950, 1st edn., p. 121.

<sup>10</sup> E. J. Seus and C. V. Wilson, *J. Org. Chem.*, 1961, **26**, 5243.

<sup>1</sup> Part 37, J. C. J. Bart and G. M. J. Schmidt, *Israel J. Chem.*, 1975, **13**, 23.

<sup>2</sup> J. D. Hung, M. Lahav, M. Luwisch, and G. M. J. Schmidt, *Israel J. Chem.*, 1972, **10**, 585.

<sup>3</sup> M. D. Cohen, R. Cohen, M. Lahav, and P. L. Nie, *J.C.S. Perkin II*, 1973, 1095.

<sup>4</sup> Z. Ludmer, Ph.D. Thesis, Weizmann Institute of Science, 1974; M. D. Cohen in 'Reactivity of Solids,' eds. J. S. Anderson, M. W. Roberts, and F. S. Stone, Chapman and Hall, London, 1972.

$M/e$  262, 192, and 165;  $\lambda_{\max}$  (EtOH) 335 nm ( $\epsilon$   $2.5 \times 10^4$ ) (Found: C, 68.4; H, 4.7; Cl, 26.8.  $C_{15}H_{12}Cl_2$  requires C, 68.5; H, 4.6; Cl, 27.0%). This material was found to be dimorphic (Table 1). Form A is obtained from solution or by quenching the melt and is isomorphous with the bromo-derivative (2). The m.p. by differential scanning calorimetry (d.s.c.) is 59°. Form B was first obtained by zone refining, and the m.p. by d.s.c. is 67°. The two forms are distinguishable by their fluorescence (they give different excimer emissions). This difference, the structure of the photodimer from A, and the fact that form B dimerises rapidly even at 77 K to give the centric photodimer, suggest that A has a 'stack' structure and B a 'pair' structure; <sup>11,12</sup> this is consistent with the cell constants.

3'-Bromo-2,4-dichloro-trans-stilbene (2) precipitated (50% yield) from the reaction mixture of the phosphonate with 3-bromobenzaldehyde. Filtration and crystallisation (ethanol) gave needles, m.p. 102–103°;  $\nu_{\max}$  (KBr) 956 and 963  $cm^{-1}$  (*trans*-HC=CH);  $\tau$  2.3–2.9 (7 H, m, ArH), 2.95 (2 H, s, *trans*-HC=CH);  $m/e$  326, 212, and 177;  $\lambda_{\max}$  (EtOH) 315 nm ( $\epsilon$   $2.6 \times 10^4$ ) (Found: C, 51.1; H, 2.8; Cl, 21.5; Br, 24.2.  $C_{14}H_9BrCl_2$  requires C, 51.3; H, 2.8; Cl, 21.6; Br, 24.4%). Constants for crystals (from ethanol) are given in the Table.

**Techniques.**—Samples of the stilbenes were prepared and irradiated as described previously,<sup>3</sup> at 8°. The X-ray powder diagrams of both stilbene and amide systems were obtained on a Philips powder diffractometer PW 1011/02 using the  $K_{\alpha}$  line of chromium (vanadium filter). In the diagram of the line-spacings *versus* composition, when ambiguity arose we were guided by the intensity behaviour: thus the intensity of a given line decreases monotonically as the concentration of the corresponding phase decreases. (This effect is superposed on a decrease in intensity as the mole fraction of the heavier molecule increases.) Typical line widths (full width at half maximum) were  $\delta(2\theta)$  ca. 0.15°; the signal-to-noise ratio varied from >60 for strong lines down to ca 3 for the weakest lines plotted. The phase diagrams were determined with a Perkin-Elmer DSC1B scanning calorimeter. Analysis of the photodimers from the stilbenes was by g.l.c. (chloroform solution; Varian 1200, flame ionisation detector; 100 cm. column with 10% SE30 on Chromosorb W30/60; injector 250 and detector 300°; temperature programmed at 10°  $min^{-1}$  from 140 to 200° and 4°  $min^{-1}$  from 200 to 270°). The monomers appeared between 150 and 180° and the dimers between 250 and 270°. It was found that for the two stilbene homodimers the ratio of peak areas in the g.l.c. was proportional to the ratio of input concentrations; the same was assumed to be true for the heterodimer.

## RESULTS

**The System *p*-chlorocinnamamide (*pcc*) + 2-(2-Thienyl)acrylamide (*taa*).**—The crystallographic constants of the monomers are in the Table. The Bragg angles for the X-ray powder lines for various compositions of the material are shown in Figure 1. In Figure 2 are given the d.s.c. results and the phase diagram constructed from them. These two sets of results are not entirely consistent with one another: the phase diagram suggests the existence of a third solid phase (peritectic) of composition ca. 50%, but no corresponding powder lines were observed.

**The System Stilbene (1) + Stilbene (2).**—Depending on the

method of preparing the sample various proportions crystallised in phases corresponding to the form A and B of (1).

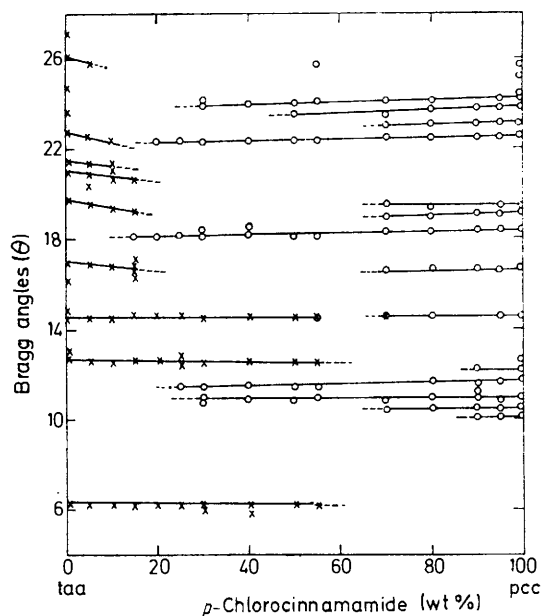


FIGURE 1 X-Ray powder reflections for the system *p*-chlorocinnamamide + 2-(2-thienyl)acrylamide

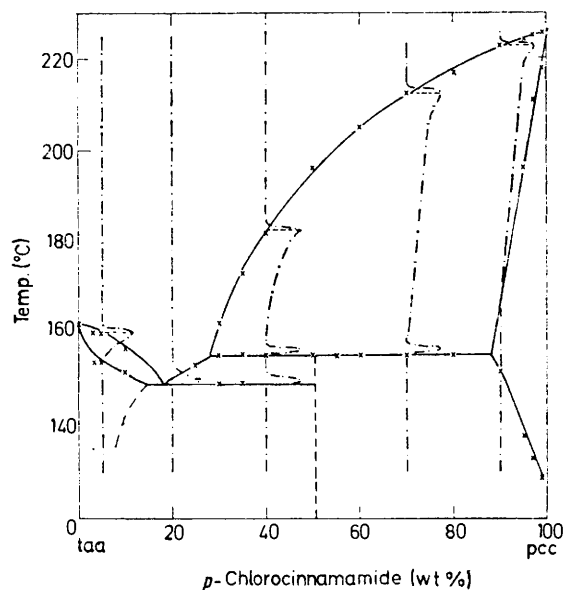


FIGURE 2 The phase diagram for the system *p*-chlorocinnamamide + 2-(2-thienyl)acrylamide, and some of the d.s.c. results (— · — · —) on which the diagram is based. The broken curve is assumed

We required all material in form A because of the isomorphism with (2); this was achieved, holding the mixture for some minutes at  $> 10^\circ$  above its m.p., and cooling slowly. Materials prepared in this way gave the results shown in Figures 3 and 4. Since the phase diagram shows that there is appreciable solid solubility the absence of shifts in the powder lines with change in composition was surprising. We

<sup>11</sup> R. Cohen, Z. Ludmer, and V. Yakhot, *Chem. Phys. Letters*, 1975, **34**, 271.

<sup>12</sup> M. D. Cohen, Z. Ludmer, and V. Yakhot, *Phys. Stat. Solidi*, 1975, **B67**, 57.

therefore made some single-crystal measurements: a large crystal specimen of (1) and (2), having varying composition along its length, was grown by zone refining. From this small crystals were cut, analysed by X-rays, and by g.l.c., to give the chemical composition. The results are in the Table.

Unit cell parameters of monomer crystals

Monomer	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )	<i>Z</i>
Stilbenes							
(1A)	<i>P2<sub>1</sub>/c</i>	13.03	4.06	24.53	90.5	1 297	4
(2)-(1)	<i>P2<sub>1</sub>/c</i>	13.20	4.00	25.10	92.0	1 325	4
(1 : 1 mol/mol)							
(2)-(1)	<i>P2<sub>1</sub>/c</i>	11.10	4.00	29.30	94.5	1 297	4
(7 : 3 mol/mol)							
(2)	<i>P2<sub>1</sub>/c</i>	11.12	3.92	29.44	95.0	1 278	4
(1B)	<i>P2<sub>1</sub>/a</i>	16.69	10.61	7.59	106.5	1 289	4
Cinnamides							
pcc *	<i>P2<sub>1</sub>/c</i>	11.00	9.08	9.04	108.4	857	4
taa †	<i>Pbca</i>	9.14	8.18	20.13		1 518	8

\* Ref. 13. † Ref. 14.

Irradiation of (1A) gave dimer (3) (93%) with traces of *cis*-monomer. The dimer was isolated by dry column

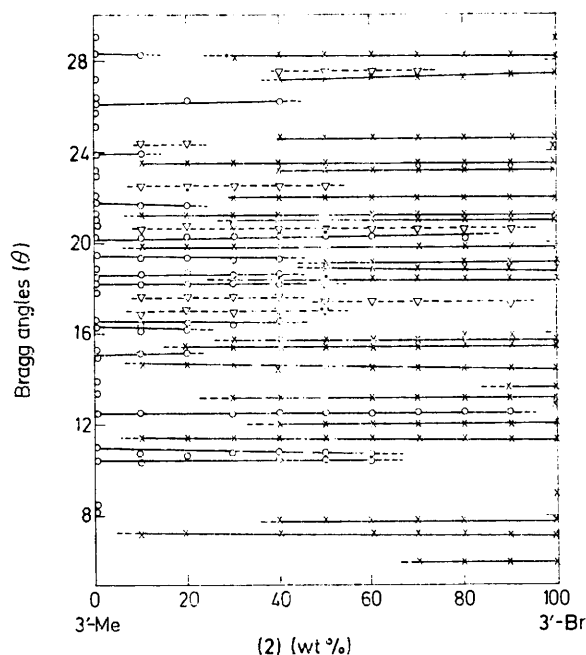


FIGURE 3 X-Ray powder reflections for the system 2,4-dichloro-3'-methyl- (1) + 2,4-dichloro-3'-bromo-*trans*-stilbene (2)

chromatography with hexane as eluant; it has m.p. 145–146° (ethanol) and proved to be the expected mirror symmetric compound *r*-1,*c*-2-*bis*-2,4-*dichlorophenyl*-*t*-3,*t*-4-*di*-3-*tolylcyclobutane* (Found: C, 68.6; H, 4.6; Cl, 26.7.  $C_{30}H_{24}Cl_4$  requires C, 68.5; H, 4.6; Cl, 26.9%);  $\tau$  (CDCl<sub>3</sub>) 2.7–3.2 (14 H, m, aromatic), 5.0–5.8 (4 H, m, cyclobutane), and 7.8 (6 H, s, CH<sub>3</sub>); *m/e* 524, 316, and 208. The stereochemical assignment is based on these data and on application of the method of mid-points in n.m.r.<sup>15</sup> Form B of (1) yielded the centrosymmetric photodimer (50%), *r*-1,*t*-3-*bis*-2,4-*dichlorophenyl*-*t*-2,*c*-4-*di*-3-*tolylcyclobutane* (6), to-

<sup>13</sup> D. Rabinovich, *J. Chem. Soc. (A)*, 1969, 2361.

<sup>14</sup> L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc. (A)*, 1969, 2372.

<sup>15</sup> D. A. Ben-Efraim and B. S. Green, *Tetrahedron*, 1974, **30**, 2357.

gether with traces of (3). Dimer (6) has m.p. 139–150° (ethanol),  $\tau$  2.5–3.1 (m, aromatic), 5.25–5.5 (m, cyclobutane), and 7.8 (s, CH<sub>3</sub>); *m/e* 524 and 262. The stereochemical assignment is based on these data and application of the method of Ben-Efraim and Green.<sup>15</sup>

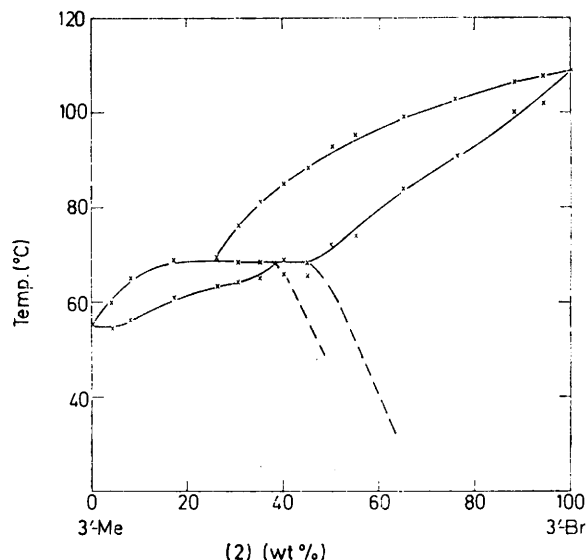


FIGURE 4 The phase diagram for the system 2,4-dichloro-3'-methyl- (1) + 2,4-dichloro-3'-bromo-*trans*-stilbene (2), based on d.s.c. results. The broken curves are assumed

Irradiation of (2) gave traces of *cis*-monomer, and, in 67% yield, (4), the mirror symmetric dimer *r*-1,*c*-2-*bis*-2,4-*dichlorophenyl*-*t*-3,*t*-4-*bis*-3-*bromophenylcyclobutane*, m.p. 125–126° (ethanol) (Found C, 51.4; H, 2.9.  $C_{28}H_{18}Br_2Cl_4$  requires C, 51.3; H, 2.8%);  $\tau$  2.6–3.1 (14 H, m, aromatic) and 5–5.8 (4 H, m, cyclobutane); *m/e* 652, 336, and 316. The stereochemistry is as for (3).

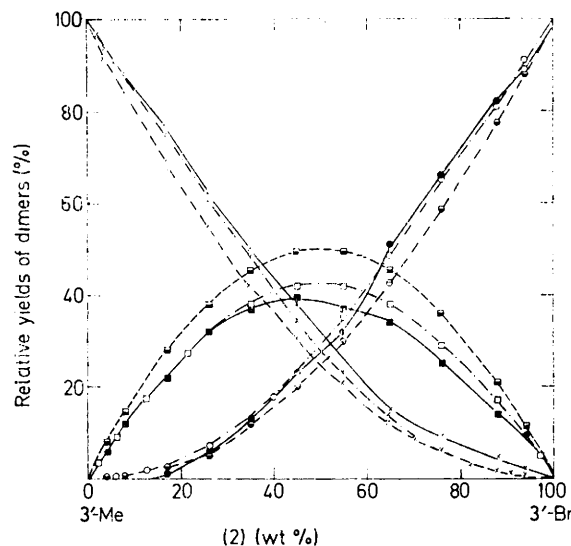
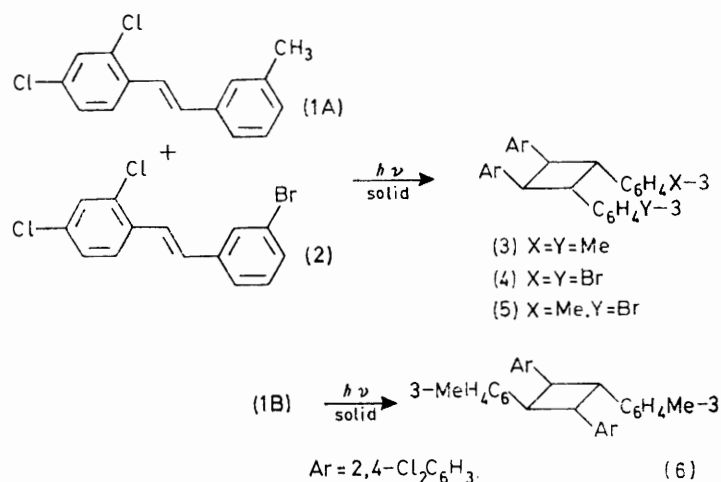


FIGURE 5 Relative yields of photodimers from the system, 2,4-dichloro-3'-methyl- (1) + 2,4-dichloro-3'-bromo-*trans*-stilbene (2). Circles, dibromo-homodimer; cross, dimethyl-homodimer; squares, heterodimer. Full lines, experimental; broken lines, calculated assuming random solid solution; dot-dash, calculated assuming solid solution with some self-aggregation

Irradiation of (1A) + (2) gave three dimers, (3), (4), and the pseudomirror symmetric heterodimer *r*-1,*c*-1-2-*bis*-2,4-dichlorophenyl-*t*-3-(3-tolyl)-*t*-4-(3-bromophenyl)cyclobutane (5). These were separated and isolated chromatographically. The heterodimer was obtained as an oil with  $\tau$  2.7–3.2 (m, aromatic), 5.1–5.7 (m, cyclobutane), and 7.8 (s, CH<sub>3</sub>); *m/e* 588, 326, and 262.

Mixtures of known compositions in (1) and (2) were irradiated. After various times samples were taken and analysed by g.l.c. The relative yields thus obtained were extrapolated back to zero time,<sup>3</sup> giving the values used in Figure 5. Making the same assumption as previously,<sup>3</sup> and



allowing for differential absorption of light by using *m* 0.987 from the spectra in solution, we calculated the expected relative yields shown in Figure 5. We find, as in the acrylic acids and amides, reasonably good agreement between the two curves.

For comparison, a benzene solution containing equal concentrations of stilbenes (1) and (2) was irradiated. By n.m.r. and g.l.c. we detected five dimers, (3)–(5) and the two centrosymmetric cyclobutane homodimers.

*The System trans-Stilbene + 3,4-Dichloro-trans-stilbene.*<sup>16</sup>—Solid mixtures containing 20, 50, and 80% of *trans*-stilbene were prepared from the melt and irradiated at +8 and –20°. At the higher temperature the material is partially molten and some dimerisation occurs. Irradiation at the lower temperature for two months gave no dimer.

#### DISCUSSION

The present results show that photodimerisation does not occur in materials of  $\gamma$ -type structure nor in their eutectics, and in the labile stilbenes the reaction is a true solid-state one and is under topochemical control. The relative yield studies lend support to our hypothesis that the locus of reaction is at or near the site of absorption of light in the bulk of phases which are random substitutional solid solutions.

The evidence supporting these conclusions is the following. First we note that both the phase diagrams and the X-ray diffraction measurements show that there is considerable mutual solubility of the two components in both systems studied. Secondly, we learn that there is

<sup>16</sup> This dichlorostilbene is non-dimerizing in the solid, B. S. Green and L. Heller, *J. Org. Chem.*, 1974, **39** 196.

nothing special about the eutectic in these systems: this follows from the behaviour of the  $\gamma$ -type materials, and from the relative yields in the photodimerisation studies which show no discontinuity in going from one- to two-phase systems, for example from 30 to 50% of the methylstilbene (1). We may conclude that these reactions occur in the bulk phase and we need seek no special mechanism for the lattice control of reaction in these cases.

It is worthwhile looking at the relative yield results for the stilbenes (Figure 5) in more detail. Throughout

almost all the composition range the homodimers are formed in yields higher than calculated, whereas the

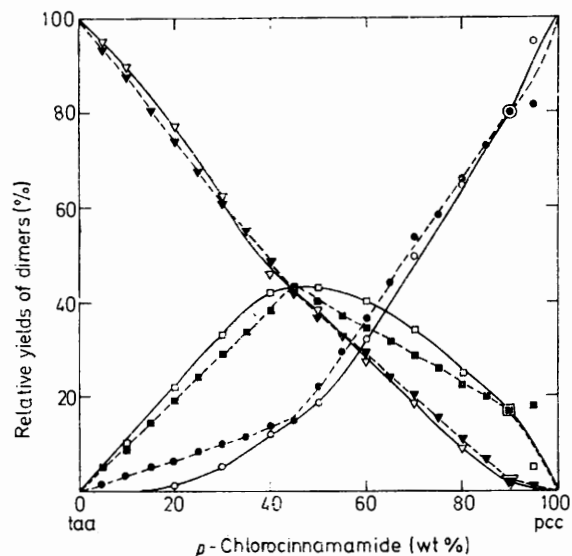


FIGURE 6 Relative yields of photodimers from the system *p*-chlorocinnamamide + 2-(2-thienyl)acrylamide. Circles, *p*-chlorocinnamamide homodimer; triangles, 2-(2-thienyl)acrylamide homodimer; squares, heterodimer. Full lines, experimental;<sup>3</sup> broken lines, calculated assuming the three dimers are produced from different phases (see text)

converse is true of the heterodimer. This suggests that the solid solutions are not perfectly random substitutional ones but that there is a preference for like

molecules to sit near one another in both crystal structures. In the kinetic treatment this is equivalent to a higher rate constant for combination of like monomers and a lower rate constant for unlike monomers. Assuming that the relative rate constants for homo- and heterodimer formation are 1.15 and 0.85, respectively, we obtain a different set of calculated relative yields (Figure 5). The differences between these yields and the experimental ones are now well within experimental error through most of the range of composition. We could obtain a further apparent improvement by assuming the tendency to self-aggregation to be higher in the phase based on the bromostilbene (2) than in that based on the methyl derivative (1). However, it is not clear that such an assumption is justified, particularly since no allowance has been made for differences in the electronic properties, such as inter-system crossing rates of the two components.

It emerges from this discussion that our model is a fairly accurate one, since only small deviations from 'ideality' are required to achieve excellent fit of calculated yields to experimental ones.

An ambiguity arises in the acrylamide system. In the

phase diagram there are indications of a phase of intermediate composition, whereas we see no sign of this in the X-ray data (room temperature). We must assume that this phase either is not formed on rapid cooling or resolves into its components on cooling to the low temperature. Let us, nevertheless, consider an alternative kinetic model based on the assumed presence of three solid phases, of compositions 0, 45, and 90% 2-(2-thienyl)acrylamide. We calculate the expected relative yields for this system and compare them with the experimental ones (Figure 6). The agreement is again reasonable and remains so even if one considers the compositions to be 0, 45, and 100%. Thus the kinetic results for this system are satisfied by a model which takes the homodimers to be formed only from the pure phases and the heterodimer only from the intermediate phase. While the weight of the evidence is against this interpretation, this points out the inadequacy of assigning a mechanism on the basis of yield studies only. In order to eliminate the possible ambiguity it is our intention to carry out similar studies on single-crystal specimens.

[5/1832 Received, 3rd September, 1975]

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