Topochemistry. Part XXXVI.[1] Relative Yields of Photodimers from Mixed Crystals of *trans*-Cinnamic Acids and *trans*-Cinnamides

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The relative yields of the photodimers from mixed crystals of various acrylic acids and acrylamides have been determined as functions of the wavelength of the exciting light and of the composition of the mixed crystal. In one system the yields were also determined for various times of irradiation. The yield *vs.* composition data were compared with data calculated on the basis of various assumptions as to the structures of the mixed crystals and the mechanism of the reaction. The wavelength effect and the fair agreement of measured and calculated yields for different compositions show that the reaction involves one excited and one non-excited molecule, and occurs at or near the site of absorption of light. Crotonic acid and amide are considered to react only as ground state partners in the reaction.

IN the previous Part[1] the applicability of the topochemical principle to mixed-crystal systems was demonstrated. The results were interpreted to indicate that in such systems there are obtained all possible products of the stereochemistry dictated by the parent phase. In the light of this interpretation one expects to be able to derive significant information on the mechanism of photodimerisation in crystals from quantitative studies on the reaction. The only kinetic results available are those of Rennert and his co-workers;[2] these authors report that the rates of dimerisation of α- and β-*trans*-cinnamic acids vary linearly with the intensity of the irradiating light and that two monomer molecules are consumed per absorbed quantum. Thus it seems that

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[1] Part XXXV, J. D. Hung, M. Lahav, M. Luwisch, and G. M. J. Schmidt, *Israel J. Chem.*, 1972, **10**, 585.

[2] J. Rennert, E. M. Ruggiero, and J. Rapp, *Photochem. Photobiol.*, 1967, **6**, 29; J. Rennert, *Photographic Science Engineering*, 1971, **15**, 60, cited in 'Photochemistry,' Specialist Periodical Report, Volume 3, The Chemical Society, London, 1972, p. 451.

the dimerisation step involves combination of an excited with a non-excited molecule, although some caution should be exercised here because of difficulties in the measurements due to scattering of light.

Consider two types of molecule, A and B, which constitute a mixed crystal which undergoes topochemically controlled photodimerisation, and let us assume that an exciting photon is initially absorbed by a B molecule. Then, depending on the nature of the neighbours of this B, a one-quantum reaction would give rise to B_2 or AB. Alternatively, however, the excitation energy may be transferred from the site of absorption; as long as it is confined to B molecules the reaction can give rise to the same products only; if the energy is transferred to an A molecule then A_2 and AB can be formed. This is based on a model of a more-or-less random solid solution. However, suppose that the true structure of the mixed crystal is one in which aggregates of, for example, B molecules are embedded in the A crystal. Then the products of reaction would be essentially only A_2 and B_2, with very little AB. Thus, from studies on the relative yields of products one can get information on the microstructure of the parent phase, on the mechanism of the reaction and on the role of transfer of energy. We here describe some studies of this sort on *trans*-cinnamic acids and amides.

EXPERIMENTAL

Samples were prepared by cooling melts from mixtures of the two components. They were powdered and spread out in Petri dishes and irradiated through Pyrex with light from Westinghouse sunlamps. (These lamps have zero output at $\lambda < 280$ nm; the intensity rises continuously from 280 to 320 nm and drops rapidly at longer wavelength. The cinnamic acids and amides in solution have absorption maxima at 260—280 nm and the long-wavelength cut-off at 310—330 nm; the thiophen derivatives have maxima at *ca.* 300 nm and the cut-off at 360 nm.) In some cases the light was filtered; suppose B has longer-wavelength absorption cut-off than does A, then by filtering through suitable Corning glasses with thin sandwiches of crystalline A between Pyrex cover slips it was possible to obtain exciting light which was absorbed by B only.

The relative yields of dimers were obtained by g.l.c. For this purpose both acids and amides were first converted into the corresponding methyl esters by methanolic HCl or by CH_2N_2. Ethyl acetate solutions of the esters were injected into a Perkin-Elmer vapour phase chromatograph using a flame ionisation detector and temperature programming. Columns were 80—100 cm and packed with 6% FFAP in Chromosorb G A/W DMCS 80/100. Monomers generally appeared at 100—150° and dimers between 220 and 260°.

All the acid and amide homodimers were known from previous work.[1,3,4] The structures of most of the heterodimers were established by Hung *et al.*[1,5]

For quantitative work the chromatograph was calibrated immediately prior to use by means of a mixture of esters of known composition. For the series of experiments with *p*-chlorocinnamamide with β-2-thienylacrylamide the yields of the esterifications were determined so that it was possible to translate the g.l.c. peak areas directly into relative yields of dimers. In the other cases it was assumed that the percentage yield of ester was the same for each dimer in an irradiated mixture.

RESULTS

Cinnamic Acids.—p-*Methoxycinnamic acid and* p-*methylcinnamic acid.* The separate components are known only in γ and α crystal structures, respectively. This system was investigated for a 1 : 1 mixture; *X*-ray powder photographs show lines of the two components' phases and some additional lines which were not identified. Irradiation with filtered (6 weeks) or unfiltered (3 weeks) light gave the following dimers in the respective proportions shown: *p,p'*-dimethyl-α-truxillic acid (*c*-2,*t*-4-bis-*p*-methylphenylcyclobutane-*r*-1,*t*-3-dicarboxylic acid) 0·044, 0·88; *p*-methoxy-*p'*-methyl-α-truxillic acid 1·62, 2·47; and *pp'*-dimethoxy-α-truxillic acid 1·00, 1·00. The light was filtered through Corning glass filter No. 5120 (transmits light of $\lambda >$ 360 nm) with sandwiches of the methylcinnamic acid.

p-*Methoxycinnamic acid and* p-*chlorocinnamic acid.* The separate components are known only in γ and β crystal structures, respectively. This system was investigated for a 1 : 1 mixture. *X*-Ray powder photographs show lines of the two known phases with some additional lines which were not identified. Irradiation with filtered (6 weeks) or unfiltered (average of results for 3, 6, and 10 days) light gave the following major products in the respective proportions shown: *pp'*-dichloro-β-truxinic acid (*t*-3,*t*-4-bis-*p*-chlorophenylcyclobutane-*r*-1,*c*-2-dicarboxylic acid) 0·10, 0·99; *p*-chloro-*p'*-methoxy-β-truxinic acid 0·64, 1·34; *pp'*-dimethoxy-β-truxinic acid 1·00, 1·00. In some cases traces of other products were also formed which were not identified. The light was filtered through the same Corning filter as above with sandwiches of the chlorocinnamic acid.

Cinnamic acid and p-*methylcinnamic acid.* Cinnamic acid is known in α(stable) and β(unstable) crystal structures,[3] and the *p*-methyl derivative only in an α structure. The system was investigated for a series of different compositions. *X*-ray powder photographs show lines of α-cinnamic acid for composition from 30 to 90% cinnamic acid, and lines of methylcinnamic acid from 0 to 70% cinnamic acid. For the composition range measured (0 to 90% cinnamic acid) three products were obtained: α-truxillic acid (*A*), *p*-methyl-α-truxillic acid (*B*), and *pp'*-dimethyl-α-truxillic acid (*C*). The relative proportions of the esters of these products, normalised to 100%, are shown in Figure 1.

β-*Substituted Acrylamides.*—Three pairs of acrylamides were studied, all with components known only in the α modification of the crystal.

β-(2-*Thienyl*)*acrylamide and cinnamamide.* The system was studied for a 1 : 1 mixture. With unfiltered light three dimers were obtained in similar yields: these dimers are α-truxillamide, its dithienyl analogue, and the thienyl–phenyl heterodimer. With light filtered through Corning glass filter No. 7380 (transmits light of $\lambda > 340$ nm) with sandwiches of cinnamamide only the second and the third dimers were formed.

β-(2-*Thienyl*)*acrylamide and* p-*methylcinnamamide.* When this system (1 : 1 mixture) was irradiated through Corning

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[3] M. D. Cohen, G. M. J. Schmidt, and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.

[4] M. Luwisch, Ph.D. Thesis, Weizmann Institute of Science, 1968 (see also ref. 1).

[5] J. D. Hung, M.Sc. Thesis, Weizmann Institute of Science, 1969 (see also ref. 1).

glass filter No. 7380 with sandwiches of *p*-methylcinnamamide the only dimers formed were the dithienyl analogue of α-truxillamide (*D*) and the thienyl-phenyl heterodimer (*E*). On irradiation with unfiltered light *pp*′-dimethyl-α-truxillamide (*F*) was formed in addition; such irradiation was performed for a series of compositions. *X*-Ray powder photographs of the starting materials showed lines of β-(2-thienyl)acrylamide in the composition range 0—60% *p*-methylcinnamamide, and lines of *p*-methylcinnamamide for compositions in the range 30—100% of the latter. For intermediate compositions (30—70%) there were some additional lines which were not identified. The yields of the three esters corresponding to the dimers, normalised to 100%, are given in Figure 2.

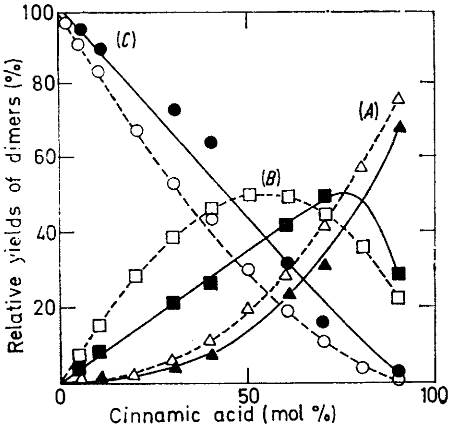


FIGURE 1 Relative yield *vs.* composition plots for the system cinnamic acid and *p*-methylcinnamic acid. Full curves, observed; broken curves, calculated

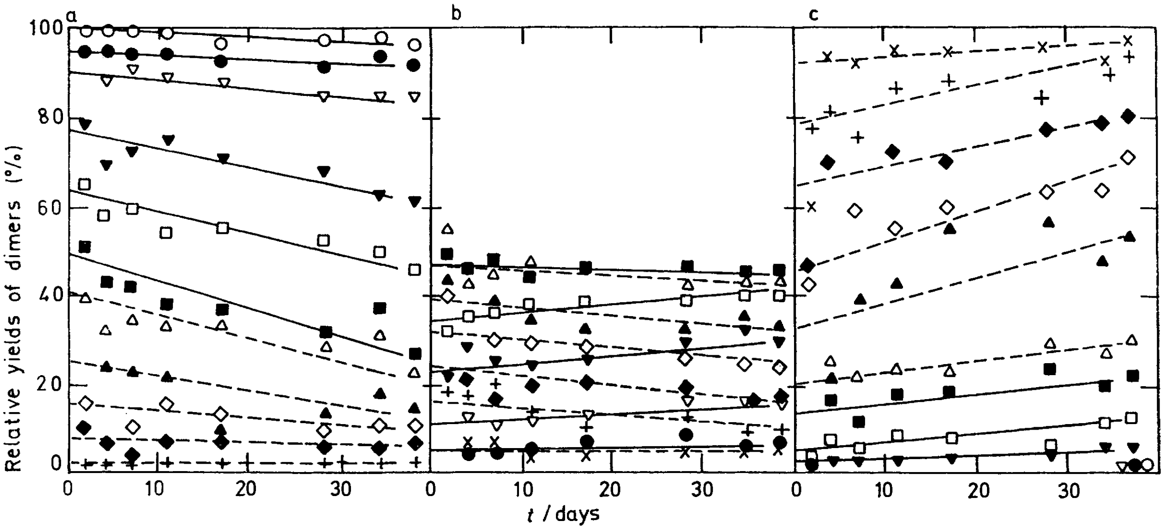


FIGURE 3 Relative yields *vs.* time for the system β-(2-thienyl)acrylamide and *p*-chlorocinnamamide; a, thienyl homodimer; b, heterodimer; c, *p*-chlorophenyl homodimer. Composition (mol % *p*-chlorocinnamamide); ○, 1; ●, 5; ▽, 10; ▼, 20; □, 30; ■, 40; △, 50; ▲, 60; ◇, 70; ◆, 80; +, 90; ×, 95. Lines for the first six concentrations are broken for clarity

β-(2-*Thienyl*)*acrylamide and* p-*chlorocinnamamide*. This particular system was investigated in the most detail. When a 1 : 1 mixture was irradiated through Corning glass filter No. 7380 with sandwiches of the cinnamamide there were obtained the dithienyl analogue of α-truxillamide (*D*) and the heterodimer (*G*). On irradiation without a filter the second homodimer, *pp*′-dichloro-α-truxillamide (*H*) was formed, in addition. Such irradiations were carried out for a series of compositions. *X*-Ray powder photographs of the samples showed lines of β-(2-thienyl)acrylamide in the composition range 0—70% *p*-chlorocinnamamide, and lines of *p*-chlorocinnamamide in the range 60—100% of the latter.

In general in these experiments the composition of the unconverted monomer changes as a result of dimerisation. In the runs described until now the relative yields of the dimers were determined after only one time of irradiation. The question then arises whether the observed yields correspond to starting concentrations of monomers or to some intermediate composition passed through during the period of irradiation. For this reason, in the system under discussion, the relative yields of the dimers were determined after various periods of irradiation. The results are shown in Figure 3. The relative yields were then extrapolated back to time zero giving the results shown in Figure 4.

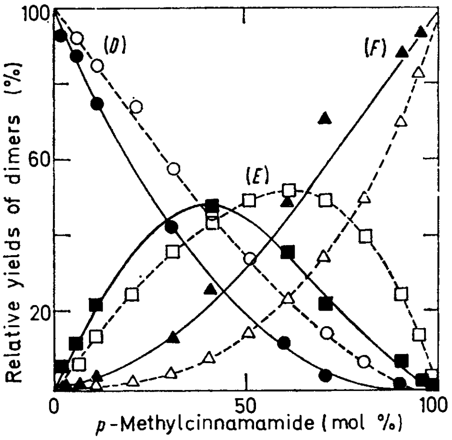


FIGURE 2 Relative yield *vs.* composition plots for the system β-(2-thienyl)acrylamide and *p*-methylcinnamamide. Full curves, observed; broken curves, calculated

Systems with Crotonamide.—Irradiation was, as above, with Westinghouse sunlamps.

Crotonamide and p-*chlorocinnamamide*. These two substances are known only in the α crystal modification. A 1 : 1 mixture shows powder lines of the two components only. The material was irradiated for 15 days, then esterified with methanolic HCl for 48 h, and the solvent and methyl crotonate were removed *in vacuo*. The oily residue was twice washed with water, dissolved in cold chloroform, and dried ($MgSO_4$). G.l.c. showed three peaks, one each of methyl *p*-chlorocinnamate, of dimethyl *pp'*-dichloro-α-truxillate, and of a mixed dimer diester. The chemical yields of these two dimer esters based on initial monomer were 6·1 and 84·2%, respectively. Irradiation of crotonamide and *p*-chlorocinnamamide (4 : 1) gave the same two dimers only.

A solution of the mixed products in ligroin–benzene (3 : 2) was passed through a column of Kieselgel 0·05—0·20, the methyl *p*-chlorocinnamate and the homodimer being eluted. When the solvent composition was changed to 2 : 3 the heterodimer was eluted. Removal of the solvent gave this dimer as an oil. Its n.m.r. spectrum ($CDCl_3$; Me_4Si internal standard) has peaks at τ 2·6—3·0 (4H, m, aromatic), 5·5—7·1 (10H, complex m overlaying two sharp s at τ 6·28 and 6·66, cyclobutane H, two different Me), and 8·78 (3H, d, *J* 7 Hz, CMe). The mass spectrum showed *m*/*e* 296 and a strong peak at 196, due to methyl *p*-chlorocinnamate.

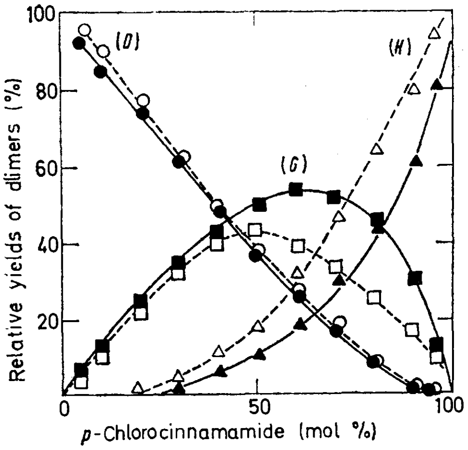
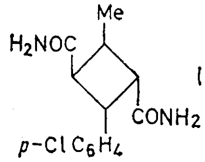


FIGURE 4 Relative yield, extrapolated to zero time, *vs*. composition plots for the system β-(2-thienyl)acrylamide and *p*-chlorocinnamamide. Broken curves, observed; full curves, calculated

Hydrolysis of the heterodimer esters with HCl–H_2O (1 : 1) for 48 h yielded a solid *diacid*, m.p. 178—180·5° (from chloroform–acetone) (Found: C, 58·3; H, 4·7; Cl, 13·2; $C_{13}H_{13}ClO_4$ requires C, 58·0; H, 4·8; Cl, 13·2%), τ [$(CD_3)_2CO$] 2·72 (4H, s, aromatic), 5·5—7·0 (4H, complex m, cyclobutane H), and 8·75 (3H, d, *J* 7 Hz, CMe).

The n.m.r. spectra of the ester and acid both fit a heterodimer with a cyclobutane ring since they show aromatic, cyclobutane, and methyl hydrogen signals. The position of the methyl signals correspond to those found in spectra of methylcyclobutanes (*e.g.* the dimers from sorbic acid and sorbamide).[6] Further, the ester has two distinct CO_2Me groups and is thus not symmetric. The signal from one of these groups has the same chemical shift as that from the CO_2Me groups of dimethyl *pp'*-dichloro-α-truxillate.[1] The corresponding group must lie *cis* to an adjacent aryl group, the second CO_2Me must be in either a 1,3- or a 1,2-*trans*-relation to the aryl. Treatment of the acid with acetic anhydride gave an open anhydride ($\nu_{max.}$ 1800 and 1700 cm^{-1}) and not a five-membered cyclic anhydride.

This evidence limits the number of possible structures of the heterodimer. Of these only one, namely (I), is formed directly from two *trans*-molecules; the others require a *trans–cis* isomerisation prior to the cycloaddition step. No example of such two-step photodimerisation reactions in the solid has been found. Further, the structure of (I) is compatible with that of the homodimer obtained from the system and no *cis*-monomer was found amongst the products. We conclude that the heterodimer is probably of structure (I).



(I)

The long-wavelength cut-off of the u.v. absorption of crotonamide is at *ca*. 260 nm. This compound therefore probably absorbs none of the light from the sunlamps and this would explain the absence of crotonamide homodimer. Solid crotonamide was irradiated for 14 days with a low pressure mercury lamp (Philips TUV 15 W; main output at 254 nm). No dimer was found. There remains the possibility that 254 nm light both forms and splits dimer, *i.e.* that a photoequilibrium is established which lies very much to the side of monomer. This possibility could be checked by exposing the dimer, if available, to the above light; unfortunately the dimer is not available. However, the heterodimer (I) was exposed to the 254 nm radiation for 14 days with no sign of decomposition.

Crotonamide and Cinnamamide. A 1 : 1 mixture, *X*-ray powder photographs of which showed lines only of the known phases of the two components, was irradiated for 30 days. The mixture was then esterified and treated further as in the previous section. G.l.c. analysis indicated three major products, methyl cinnamate, dimethyl α-truxillate, and a heterodimer. This heterodimer diester has the same retention time as the product of dehydrochlorination and methylation of the heterodimer diacid from crotonamide and *p*-chlorocinnamamide. The heterodimer is thus probably the dimethyl ester of *c*-2-methyl-*t*-4-phenylcyclobutane-*r*-1,*t*-3-dicarboxylic acid.

DISCUSSION

Effect of the Wavelength of the Irradiating Light.—Because the two components have different absorption spectra it is possible to excite both or, by use of suitable cut-off filters, only the one with the longer wavelength absorption cut-off. Several examples, all 1 : 1 mixtures, have been given. In all cases not involving crotonamide or crotonic acid, three dimers (2 homo and 1 hetero) are formed with unfiltered light. With filtered light the homodimer of the 'non-absorbing' component

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[6] B. S. Green, M. Lahav, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1971, 1552.

is hardly formed at all, and its relative yield drops with increasing thickness of the sandwich filter; it is reasonable to assume that none of this dimer would be formed if the light filtration were completely effective. Furthermore the ratio of the amount of heterodimer formed to that of homodimer formed drops by approximately half on passing from unfiltered to filtered light. A marked wavelength dependence of relative yields with wavelength was found even for the system *p*-chloro- and *p*-methyl-cinnamamide where the absorption spectra were very similar.

Note that these results are obtained even when *p*-methoxycinnamic acid is one of the components, *i.e.* when one phase is non-reacting. In such cases we obtain only those products which originate from the second phase. The wavelength effect is therefore not due to changes in the proportions of the light absorbed by the two phases, but to changes in the proportions of the light absorbed by the two components of the reactive phase.

If A and B are the two components, and B has the longer wavelength cut-off, then the above results suggest that the reactions can to a first approximation be described by processes (1)—(6).

For unfiltered light

$$A \xrightarrow{h\nu} A^* \qquad B \xrightarrow{h\nu} B^* \qquad (1)$$

$$A^* + A \longrightarrow A_2 \qquad B^* + A \longrightarrow AB \qquad (2)$$

$$A^* + B \longrightarrow AB \qquad B^* + B \longrightarrow B_2 \qquad (3)$$

For filtered light

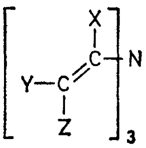
$$B \xrightarrow{h\nu} B^* \qquad (4)$$

$$B^* + A \longrightarrow AB \qquad (5)$$

$$B^* + B \longrightarrow B_2 \qquad (6)$$

We do not know whether the cycloaddition occurs from the singlet or triplet excited state of the monomer. Qualitatively we can tell from the results with filtered light that excitation energy is not reaching A from B; from the experiments with unfiltered light we conclude that neither of the components is trapping a dominant part of the excitation energy. Consideration of the various possible mechanisms leads us to conclude as follows: the reaction may proceed from the first singlet excited state at a rate which is larger than that of transfer of energy; alternatively, the reaction proceeds from the triplet state, with intersystem crossing being faster than transfer of singlet excitation energy, and with reaction being faster than triplet energy transfer. In either case reaction occurs at or near the site of absorption of light.

One other factor, which has been implicitly assumed above, is established by these experiments. We note that when B only is excited both AB and B_2 are formed. Since the energy is not transferred from B to A, the only pathway to AB is $B^* + A \longrightarrow AB$. Thus, the reaction involves combination of an excited molecule with a ground state molecule, in keeping with the conclusions of Rennert and his co-workers.[2]



(II)

Systems containing Crotonic Acid or Crotonamide.—We have shown that crotonamide does not undergo photodimerisation in the crystal, even though the structure is suited to such a reaction.[7] This is true even when strongly absorbed light (254 nm) is used, and is probably not due to an unfavourable photoequilibrium; it seems rather that photodimer is not formed at all.

Crotonic acid also does not photodimerise [8] despite its crystal structure.[9] In this context the results of LaLonde and Davies [10] are of interest. These authors irradiated the amine (II) in solution. The compounds with X = Me, Y = H, Z = H, with X,Y = $[CH_2]_4$, Z = H and with X,Y = $[CH_2]_3$, Z = H all underwent intramolecular cyclisation to cyclobutane derivatives. However, in the absence of the α-methyl group, as in the compounds with X = H, Y = Me, Z = H and with X = H, Y = Me, Z = Me, no cyclisation occurred. LaLonde and Davies suggest that α-substituted materials adopt a non-planar configuration in which the double bonds are close to one another, whereas the other substances adopt an open, planar configuration in which the double bonds are well separated. The fact that the latter compounds do not react and that the former react with retention of the *transoid* configuration is taken as evidence that the excited state involved is a very short-lived one, presumably a singlet. A triplet intermediate would be of biradical character and would lead to partial inversion of configuration.[11]

Our results show that in mixed crystals containing crotonic acid or its amide mixed dimers are obtained together with the homodimer of the second component. Our explanation for this is that crotonic acid and amide can act only as the ' ground state partner ' in the photocyclisation. Thus, if the reaction proceeds from the singlet state this state must be of very short lifetime in these substances. If, on the other hand, the reaction proceeds from the triplet state, then the rate of intersystem crossing must be very low, and/or the triplet lifetime is very short.

Relative Yields vs. *Composition Curves*.—We enquire whether we can reproduce the experimental yield

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[7] J. C. J. Bart, L. Leiserowitz, and G. M. J. Schmidt, unpublished results cited by L. Leiserowitz and G M. J. Schmidt, *J. Chem. Soc.* (*A*), 1969, 2372.

[8] G. M. J. Schmidt, in ' Reactivity of the Photoexcited Molecule,' Interscience, New York, 1967, p. 227.

[9] J. M. Robertson and S. A. Sutherland, personal communication cited in ref. 8.

[10] R. T. LaLonde and C. B. Davis, *Canad. J. Chem.*, 1969, **47**, 3250.

[11] L. Salem and C. Rowland, *Angew. Chem.*, 1972, **11**, 92, and references cited therein.

curves using a simple model for the mechanism. We make the following assumptions. (a) The mixed crystals are perfectly random substitutional solid solutions. (b) There is no transfer of excitation energy between A and B molecules. (c) The steady-state concentration of excited molecules of a given component is proportional to the rate at which light is absorbed by that component.

Let us first consider a single phase. The reactions (7)—(10), with corresponding specific rate constants, occur. For the systems described in Figures 1 and 2 we

$$A^* + A \longrightarrow A_2 \quad k_{AA} \qquad (7)$$

$$A^* + B \longrightarrow AB \quad k_{AB} \qquad (8)$$

$$A + B^* \longrightarrow AB \quad k_{BA} \qquad (9)$$

$$B^* + B \longrightarrow B_2 \quad k_{BB} \qquad (10)$$

take the specific rate constant as the average during the time of irradiation, while for that of Figure 4 we take the rate constants extrapolated to time zero. Then the relative yields of the dimers are given by equation (11).

$$[A_2] : [AB] : [B_2] = k_{AA}[A^*][A] : (k_{AB}[A^*][B] + k_{BA}[A][B^*]) : k_{BB}[B^*][B] \qquad (11)$$

The steady-state concentration of excited component i, according to assumption (c), is given by (12) where $I(\lambda)$

$$[i^*] = \text{const.}\ [i]\int I(\lambda)\ \varepsilon_i(\lambda)\ \mathrm{d}\lambda \qquad (12)$$

is the intensity of the light from the sunlamp as a function of wavelength, and was obtained from maker's specifications. The extinction coefficient $\varepsilon_i(\lambda)$ is taken to be that of solution. Then the relations (13) and (14) are obtained where the m were evaluated numerically

$$\frac{[B^*]}{[A^*]} = \frac{[B]\int I(\lambda)\ \varepsilon_B(\lambda)\ \mathrm{d}\lambda}{[A]\int I(\lambda)\ \varepsilon_A(\lambda)\ \mathrm{d}\lambda} \qquad (13)$$

$$= m[B]/[A] \qquad (14)$$

for each pair of monomers. Substituting in (11) and rearranging we get (15) where $r_{ij} = k_{ij}/k_{AA}$.

$$[A_2] : [AB] : [B_2] = [A]^2 : (r_{AB} + r_{BA}m)[A][B] : r_{BB}m[B]^2 \qquad (15)$$

The expression can readily be modified to apply to a system of two phases of known compositions. Now presumably the rate constant k_{ij} is different in the two phases. We do not have data on this point; to allow us to process our data further we make the further very drastic assumption that the relative specific rate constants are the same for all reactions and in both phases. Using this assumption we have treated several cases both as single phase systems and as systems of two phases of different compositions. The results agree well so that we treat all systems as single phase ones.

We find m to be 0·645, 0·432, and 0·313 for the systems of Figures 1, 2, and 4, respectively. Equation (15) with these numbers gives the 'calculated' curves plotted in these Figures. Considering the crudity of the assumptions we have made, the agreement between calculated and experimental curves is surprisingly good. The discrepancies can well be interpreted in terms of differences between the relative specific rate constants in the two phases of the given system. However, we can conclude that to a fair approximation the other assumptions are valid: in particular to first order *we can consider the systems as consisting of random solid solutions in which little or no transfer of energy occurs prior to reaction.*

We ask whether it is possible to extract more quantitative conclusions from the data we have given. For this purpose only the results of Figures 3 and 4 are likely to be of use. First we note that for low concentrations of *p*-chlorocinnamamide the agreement between calculated and observed yields is very good; this is not so at high concentrations. This undoubtedly indicates that the rate constants are different in the phases based on the structures of the thienyl and *p*-chlorophenyl components. In the high concentration range we find that the heterodimer is formed in lower yields than expected while the converse is true of the *p*-chlorophenyl homodimer. This does not seem interpretable in terms of energy transfer; however, it could be that in this concentration range an excited *p*-chlorophenyl molecule reacts at higher rate with other *p*-chlorophenyl molecules than with thienyl molecules. A possible explanation for this is that in this particular structure there is some aggregation of the former molecules.

We conclude that several of the assumptions we have made are not strictly applicable but that our major conclusions remain valid to our degree of approximation. We are in the process of checking the mutual solid solubilities in some of the systems by direct measurements.

[2/2627 *Received, 20th November, 1972*]