cis–trans Isomerization in Solid Matrices by γ Irradiation[1]

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Abstract: The conversion of α-phenyl-*cis*-cinnamic acid to the *trans* isomer occurred in the solid phase under γ irradiation when the solid was in intimate contact with an alkali metal bromide. A similar effect was produced in contact with hexabromoethane but not with hexabromobenzene. Cuprous bromide, thallium bromide, potassium chloride, and potassium iodide were inactive. The effect is attributed to bromine atom catalysis. Potassium bromide similarly triggered the solid-state conversion of *cis*-dibenzoylethylene to the *trans* isomer but was without effect on maleic or fumaric acid. The liquid phase isomerization of dimethyl maleate under γ irradiation was subject to marked acceleration of a less specific nature by contact with various solids, thallium bromide being the most active of those tested.

During the course of an exploratory investigation of *cis–trans* interconversions in the solid state under γ irradiation, the unexpected observation was made that in certain cases the isomerization reaction can be sensitized by contact of the solid with various other materials. Isomerization reactions of the *cis–trans* type have been effected by ionizing radiations in pure liquids[2] and in solutions,[3,4] but there appears to be only one recorded instance of an isomerization in the solid state, namely, the conversion of the low-melting isomer of N-methyl-N-β-styryl-p-toluenesulfonamide to the higher-melting isomer by exposure to 2-Mev. electrons.[5]

Not surprisingly perhaps, in view of the limitation as to mechanisms operable in the solid state, the present study revealed no additional examples of reactions in pure crystalline materials. However, a chance observation on KBr pellets revealed that reaction could be effected indirectly through energy absorbed in the alkali halide phase. The effect was first encountered in α-phenyl-*cis*-cinnamic acid, m.p. 138°, which by itself is unaffected as to melting point, appearance, or infrared spectrum by γ rays at moderate dosage, but in a KBr pressed pellet shows conversion to the more stable *trans* form, m.p. 174°. Jones[6] has referred to radiolyses by transferred energy of compounds dispersed in alkali halide matrices, and indeed it was with the purpose of securing a higher effective dose that irradiation of the material in the form of KBr pellets was first tried.

When it was found that the phenomenon exhibits a strong temperature dependence, the simple picture of energy transfer between phases became less convincing. With the further finding that the effect was absent in KCl and KI pellets, it was suspected that what was being transferred was perhaps not energy but a specific chemical-sensitizing agent. A chemical-sensitizing action has been observed,[3] and attributed to bromine atoms, in the liquid-phase isomerization of *cis*-polybutadiene in solutions containing organic bromides, under γ irradiation. There appears to be no precedent for a similar effect in the solid state, and it was of interest to attempt additional confirmation and to identify, if possible, the active species. The experimental development included, first, the testing of other solid bromine compounds for sensitizing action; second, a consideration of molecular bromine and of hydrogen bromide as possible catalysts; third, the examination of some other *cis–trans* pairs, both solid and liquid, for susceptibility to a heterogeneous, bromide-ctalyzed, isomerization, and finally, a mechanistic test based on the action of an inhibitor.

Experimental Section

Materials. Commercially available α-phenylcinnamic acid, which contains approximately 5% of the lower melting isomer, was fractionated, and the crude isomers were purified by the procedure of Stoermer and Voht[7] to furnish α-phenyl-*cis*-cinnamic acid,[8] m.p. 138°, and α-phenyl-*trans*-cinnamic acid, m.p. 174°.

cis-Dibenzoylethylene, m.p. 133–134°, was produced from the commercially available *trans* isomer by exposure of a stirred suspension in methanol to sunlight until the yellow color of the *trans* isomer had disappeared. The potassium bromide was Harshaw infrared grade. Potassium chloride of both infrared and reagent grade was used without discernible difference in results. Otherwise, best available grade chemicals were used without purification.

γ-Irradiation Procedures. The first experiments with the isomers of α-phenylcinnamic acid were performed on 50-mg. samples of the pure material, and on 13-mm. KBr pellets, contained in evacuated glass vessels fitted with break-seals to permit collection of gaseous products. The production of gas was negligible, however, and when it was realized that the self-heating of samples exposed at the highest available γ flux was a contributing factor in the isomerization reactions, the practice was adopted of filling the containers with slightly less than 1 atm. of inert gas, usually argon, after prolonged high-vacuum pumping. In some early experiments, several different solid specimens were mounted on a rack within a cylindrical steel container fitted with a center well into which the Co-60 slug was lowered. This arrangement, though it permitted a symmetrical arrangement of samples around, and close to, the Co-60 slug, was soon abandoned both because of heating effects and because of possible cross-contamination of specimens. The technique then adopted was to place three similar specimens in an aluminum holder held between glass wool plugs in a glass ampoule. The sealed glass ampoules were placed within tubular metal holders at available positions at distances of 3 cm., or a multiple thereof, from the central source position.[9] When the specimens were to

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] A. Charlesby, *Radiation Res.*, **2**, 96 (1955).

[3] M. A. Golub, *J. Am. Chem. Soc.*, **80**, 1794 (1958); **81**, 54 (1959).

[4] R. B. Cundall and P. A. Griffiths, *Discussions Faraday Soc.*, **36**, 111 (1964).

[5] F. W. Stacey, J. C. Sauer, and B. C. McKusick, *J. Am. Chem. Soc.*, **81**, 987 (1959).

[6] A. R. Jones, *J. Chem. Phys.*, **35**, 751 (1961).

[7] R. Stoermer and G. Voht, *Ann.*, **409**, 36 (1915).

[8] In this paper we adhere to the system of naming these compounds as derivatives of *cis*- or *trans*-cinnamic acids. The literature on this point is confusing. Thus the lower melting isomer is referred to as "*trans*-α-phenylcinnamic acid" [L. F. Fieser, *J. Chem. Educ.*, **31**, 293 (1954)] and as *trans*-stilbene-α-carboxylic acid [J. D. Berman and C. C. Price, *J. Am. Chem. Soc.*, **79**, 5474 (1957)].

[9] The source has been described by R. A. Blomgren, Proceedings of the Sixth Hot Laboratories and Equipment Conference, 1958, p. 229. The effective loading during the period of the work described herein was approximately 2000 curies.

be maintained above ambient temperature, the tubular holder was wrapped with heating tape and, with the aid of thermocouples, temperatures were adjusted and maintained manually within ±1°.

Most of the exposures were done at dose rates ranging from 12 × 10^{20} e.v./l. min., at a 3-cm. distance, to 1.5 × 10^{20} e.v./l. min., at a 12-cm. distance from the source center. There was initially some uncertainty, greatest for exposures at the 3-cm. position, from the fact that the solid specimens presented a geometry different from the liquid specimens used in Fricke dosimetry. Attempts to use cesium nitrate, in the form of pressed pellets, as a solid dosimeter[10] were abandoned because of gross discrepancies in nitrite yields as compared with literature values. Another type of solid-state dosimeter, based on the fading of a blue cellophane,[11] was useful for locating zones of uniform flux but was unsatisfactory for the estimation of absolute doses. The uncertainty was eventually dispelled through the use of microcells of appropriate dimensions for Fricke dosimetry which provided excellent confirmation of the original dosimetry.

Analytical Methods. The analytical determination of the *cis*- and *trans*-α-phenylcinnamic acid mixture was based on infrared measurements (7.3- and 15.7-μ peaks for the *cis* isomer, and 8.45- and 12.73-μ peaks for the *trans*) on 200-mg. pellets with a fixed content of organic material equal to that in calibration mixtures made up with KBr, CsBr, and NaBr to cover the whole range in 10% intervals. A similar procedure, employing only KBr pellets and measuring the 11.17-, 12.80-, and 13.65-μ peaks of the *cis* isomer against 12.47- and 15.82-μ peaks of the *trans* isomer, was followed in the determination of *cis*- and *trans*-dibenzoylethylene mixtures.

The analysis of dimethyl maleate–fumarate mixtures was by gas chromatography on a 6-ft. column of 15% Carbowax–terephthalic acid on Chromosorb W at 135°.

No one method of expressing the results is entirely satisfactory or appropriate. As Jones[6] has noted, *G* values can be based on the energy absorbed by one component or in the total energy absorbed, and may be quite different in order of magnitude. In the systems at hand the *G* values, on whatever basis calculated, will have no significance except relatively within a given series of experiments because of uncontrolled variables such as particle size and dispersion. As a somewhat arbitrary procedure, the results will be expressed as *G* values based on total dosage and as per cent *cis* to *trans* conversion. The total dose is computed as the sum of the doses to the two solid phases, each being estimated on the basis of the appropriate electron densities.

Isomerization of α-Phenyl-*cis*-cinnamic Acid. Effect of Alkali Metal Halides. A typical set of results for α-phenyl-*cis*-cinnamic acid, pelletized in KBr at various concentrations and exposed to a dose of 29.1 × 20^{20} e.v./g. at two different temperatures, is shown in Table I. While it was possible by careful adherence to a standard ritual in the fabrication of pellets to achieve reasonably consistent results within a single series of experiments, the yields were not in general well reproducible. Thus the averaged *G* values and the average deviation, in five series of experiments with pellets at 0.37–0.39% concentration, were 0.16 ± 0.04 at 70–73° and 0.14 ± 0.04 at 48–51°. At room temperature (26°) the conversion to *trans* isomer at the given doses was too low for precise estimation by the infrared method; the *G* value was of a 0.04 order of magnitude. An intimately ground, loosely packed powder, 0.38% *cis* isomer in KBr, gave conversions to *trans* isomer represented by *G* values of 0.09 and 0.08, at 48 and 72°, respectively, compared with 0.10 and 0.13 for the same material as pressed pellets.

Table I. γ Irradiation of KBr Pellets Containing α-Phenyl-*cis*-cinnamic Acid

Compn., wt. %	t = 36° % *trans*		t = 48° % *trans*	
	% *trans*	G_{trans}	% *trans*	G_{trans}
0.37	24.9	0.10	53.3	0.22
0.57	22.2	0.14	38.2	0.24
0.97	16.0	0.18	28.8	0.32
1.27	15.5	0.22	22.4	0.32
2.06	10.4	0.24	18.2	0.42
4.77			6.4	0.34

Sodium bromide, compared as pellets with potassium bromide, both at 45°, was equally effective in promoting isomerization. Cesium bromide, compared with potassium bromide at 51 and 73°, appeared to be more effective by a factor of two.

Potassium chloride, potassium iodide, and thallium bromide, tested as pellets containing 0.4% of the *cis* acid at temperatures up to 70°, were totally ineffective with respect to isomerization under γ irradiation. Cuprous bromide, at 49°, was also ineffective.

Effect of Organic Bromides. Mixtures of the *cis* acid and hexabromobenzene, as compacted powder (Parr pellet press) or as loose powder, were irradiated at room temperature and at temperatures up to 69° without evidence of conversion to the *trans* isomer except at 69° and at the highest dose, 5.8 × 10^{21} e.v./g., where a trace of *trans* isomer could be seen. In contrast, hexabromoethane, in powder mixtures with the *cis* acid, effected isomerization at 26° with *G* values ranging from 10 to 21.

Effect of Gases. The foregoing observations relate to specimens sealed under an atmosphere of argon gas. With other gases in contact with the samples, the following effects were noted. Powdered mixtures of the *cis* acid, 0.38%, in potassium bromide and in potassium chloride, were irradiated in contact with air at 51°. At the same time a sample of the powdered *cis* acid in contact with air was irradiated, all at a dose of 2.7 × 10^{21} e.v./g. The *cis* acid alone was unaltered, whereas the mixture with potassium bromide showed substantially complete conversion to *trans* and the mixture with potassium chloride was converted to the extent of 40%.

In experiments with bromine vapor in contact with 10-mg. samples of finely ground pure *cis* acid, bromine vapor was introduced to a pressure of 10 cm. from a side arm containing excess bromine, which was frozen during evacuation, by allowing the side arm to warm to −25° and then sealing. The tubes were protected from light. After 48 hr. at room temperature, the solid showed no change spectroscopically. On γ-ray exposure at a dose of 2.9 × 10^{21} e.v./g., a sample exposed at ambient source temperature (26°) showed 8.9% conversion to *trans* acid, while another sample at the same dose but maintained at 48° showed essentially quantitative conversion to *trans* acid.

Hydrogen bromide, introduced at about 200 mm. pressure by expansion from an attached U-tube containing the gas at atmospheric pressure, was allowed to remain in contact with 20–28-mg. samples of finely ground pure *cis* acid at 50° for periods of 24 and 120 hr. without effect as to melting point or infrared spectrum of the solid. The effect of γ irradiation in the presence of hydrogen bromide was not investigated.

The γ irradiation of 200 mg. of an intimate mixture of *cis* acid (0.37%) in potassium bromide, as a loose powder, in contact with allene gas was performed in a glass vessel to which was attached a Bourdon vacuum gauge. This permitted observation of the pressure at daily intervals during the irradiation through a window in the source chamber wall. The glass vessel, of approximately 100-ml. capacity, containing the solid mixture in a small open capsule, was filled with allene gas to a pressure of 630 mm. The gas was condensed in a small side arm to permit detachment of the vessel from the line by sealing at a constriction. During the γ irradiation the lower end of the vessel, in which the capsule containing solid rested, was heated under manual control at 53°. In a period of 90 hr. a dose of 3.2 × 10^{21} e.v./g. was given. During this time the gauge reading increased perceptibly from an initial 5.0 to a final 7.2 which would reflect a decrease in pressure of approximately 10%. The infrared spectrum of the recovered solid showed no detectable isomerization.

Isomerization of Dibenzoylethylene. Samples of *cis*- and of *trans*-dibenzoylethylene, in an atmosphere of argon, irradiated at 26 and at 59° to a dose of 3.1 × 10^{21} e.v./g., showed no change by infrared analysis. In potassium bromide pellets, at 0.39% concentration, the *trans* isomer was unaffected by irradiation at the same dosage at either 26 or 59°, but the *cis* isomer was converted to *trans* to the extent of 14% (G = 0.06) at 26° and virtually quantitatively in the pellets irradiated at 59°.

Isomerization of Cinnamic Acid. Qualitative observations only were made on *cis*- and *trans*-cinnamic acids which showed that the former is readily isomerized in the presence of KBr when exposed either as a powdered mixture or as a pressed pellet to γ irradiation. In this case, however, the pure *cis* isomer alone showed isomerization, detectable by infrared spectrum and representing perhaps 5% conversion to *trans* acid, at a dose of 2 × 10^{21} e.v./g. at 26°. Qualitatively, the conversion was not significantly altered by admixture of KCl, but mixtures with KBr irradiated simultaneously showed complete conversion to the *trans* isomers. The irradiation at this level of the *trans* isomer, alone or in mixtures with KCl and KBr, caused no change in the infrared spectrum.

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(10) T. Chen and E. R. Johnson, *J. Phys. Chem.*, **66**, 2249 (1962); *cf.* also *Nucleonics*, **21**, 66 (1963).

(11) E. J. Henley and D. Richman, *Anal. Chem.*, **28**, 1580 (1956).

Isomerization of Dimethyl Maleate. Mixtures of dimethyl maleate and various solid materials were made up in a constant ratio by bulk volume (50–55 mg. of dimethyl maleate to 150–300 mg. of solid) such that the liquid was just sufficient to wet the solid. The two components were degassed in separate arms of a yoke, and the arm was sealed off under vacuum. The γ irradiations were performed at 60° at doses in the range $2\text{–}5 \times 10^{20}$ e.v./g. From the standpoint of reproducibility, the observations were not wholly satisfactory. The observed G values for dimethyl fumarate production in control experiments, on 50-mg. samples of dimethyl maleate with no added solid, ranged from 3 to 7.8 and may not be truly representative of the bulk liquid because of the accelerating effect of glass. There was a twofold variation, not explicable in terms of any known variables, in the yield of fumarate in the presence of potassium bromide. Within a single series of experiments, the results are possibly more meaningful, at least relatively as, for example, the following yields of dimethyl fumarate expressed in each case, first as a G value based on the total dose, and then as a G value based on dose to the organic phase only: potassium bromide (macrocrystalline), 26.0, 79.6; potassium bromide (finely ground), 27.4, 125; potassium chloride (reagent grade, finely ground), 10.5, 37.0; thallium bromide (very fine powder), 52.6, 277; silica gel (60–80 mesh, chromatographic grade), 4.61, 29.6; Pyrex glass (80–100 mesh), 6.40, 22.4. No products other than dimethyl fumarate were observed in the gas chromatographic analysis.

The γ irradiation of maleic and fumaric acids, alone or in admixture with potassium bromide or chloride and at temperatures up to 70°, did not effect detectable interconversion of isomers.

Discussion

With one exception, namely the isomerization in the presence of KCl and air, a sensitizing effect has been seen only in compounds of bromine. This specificity provides grounds for supposing that a chemical species capable of triggering an isomerization process in the organic crystal is generated in the sensitizing solid. The bromides which show this action have no common element of composition other than bromine, and the chemical forms that might reasonably be considered include molecular and atomic bromine, ionic species, and additionally, since protons are available from the organic component, hydrogen bromide. There is an indication that a volatile species, rather than an ionic species, is involved in the observation that the sensitizing action is observed in a loose powdered mixture to nearly the same degree as in a highly compressed pellet. However, there is no measurable buildup of volatile material and there is no sensitized isomerization when the two solid powders are contained during irradiation in separate compartments within a sealed tube. A direct proof that neither hydrogen bromide nor molecular bromine is the catalytically active species is the failure of these substances to effect isomerization when in contact with the *cis* acid at pressures far greater than could possibly exist in the irradiated mixtures with KBr. By elimination, therefore, the weight of evidence favors atomic bromine as the active species.

The failure of certain bromides, *e.g.*, cuprous bromide, thallium bromide, and hexabromobenzene, to act as sensitizers is not in itself an obstacle to the proposed interpretation. There is no theoretical requirement that all solid bromides should be equally capable of emitting atomic bromine under γ irradiation, nor is there at present any suitable independent technique for the measurement of bromine atom generation.

The bromine atom hypothesis receives strong support from the inhibition of the KBr-sensitized isomerization by allene which is reported to be a very effective bromine atom scavenger.[12] It is clear, however, that the liquid-phase isomerization of dimethyl maleate, known to be subject to bromine atom catalysis,[13] was a poor choice for an independent demonstration of bromine atom generation from solids under γ irradiation. There is indeed an acceleration of isomerization from added bromides, and hence no evidence contrary to the bromine atom hypothesis, but the acceleration does not correlate with the effectiveness of different bromides in the isomerization of α-phenylcinnamic acid. Obviously no assertion can be made as to the role of atomic bromine, if any, in the liquid-phase reactions. The acceleration by inert solids, such as silica and glass, is reminiscent of the silica-sensitized polymerization of liquid styrene under γ irradiation which is believed to proceed predominantly by ionic mechanisms.[14] Further studies relating to the possibilities for initiating halogen atom chain reactions in the gas phase by the irradiation of solid halides can be expected to provide more definitive results. Gas-phase reactions initiated in this way might have an added element of practical utility in that the presence of a solid initiator could result in more effective capture of γ-ray energy than is practicable in homogeneous gas-phase reactions.

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