Crystal Lattice Photochemistry Often Proceeds in Discrete Stages; Mechanistic and Exploratory Organic Photochemistry.

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Supporting Information.

I. Solid State Photochemistry of 4-α-Naphthyl-4-β-naphthylcyclohex-2-enone **1**.

1. Exploratory Photolysis. Irradiation of fine crystalline material was performed between two quartz slides (size 5.0 x 5.0 cm) with a water-cooled medium pressure 400 W mercury-xenon lamp equipped with Pyrex filter. To prevent possible melting during photolysis samples were cooled with water to room temperature. In one experiment 50 - 75 mg of fine crystals of enone were used. At fixed times a portion (5 mg) of the sample was removed and the product ratio was determined using ^{1}H NMR. Multiple experiments were carried out and the data were combined into the following table:

Conversion	0.03	0.06	0.07	0.1	0.12	0.14	0.15	0.19
Ratio **1c** / **1d** / **1a**	2.0:1.0:0	2.0:1.0:0	4.0:1.0:0	9.5:4.0:1	9.0:3.5:1	5.7:2.3:1	8.0:2.5:1	4.3:2.0:1
Fraction of **1c**	0.02	0.04	0.06	0.07	0.08	0.09	0.10	0.11
Fraction of **1d**	0.01	0.02	0.01	0.02	0.03	0.04	0.03	0.05
Fraction of **1a**	0	0	0	0.01	0.01	0.01	0.02	0.03

Conversion	0.24	0.30	0.34	0.35	0.45	0.5	0.51
Ratio **1c** / **1d** / **1a**	5.7:2.7:1.0	5.0:2.0:1.0	4.0:2.8:1.0	3.3:1.7:1.0	4.3:3.3:1.0	3.2:3:1.0	3.6:4.0:1.0
Fraction of **1c**	0.15	0.19	0.18	0.19	0.23	0.22	0.21
Fraction of **1d**	0.07	0.08	0.12	0.1	0.17	0.21	0.24
Fraction of **1a**	0.02	0.03	0.04	0.06	0.05	0.07	0.06

Conversion	0.6	0.62	0.64	0.73
Ratio **1c** / **1d** / **1a**	3:3.2.0:1.0	2.7:3.3:1.0	3.0:3.3:1.0	2.6:3.3:1.0
Fraction of **1c**	0.25	0.25	0.26	0.29
Fraction of **1d**	0.27	0.28	0.29	0.35
Fraction of **1a**	0.08	0.09	0.09	0.11

2. Preparative Solid State Photolysis. Two 80 mg portions of enone **1** were photolyzed as described above for 40 h. The product mixture then was separated by column chromatography (silica gel, column 50×2.5 cm, ethyl acetate - hexane 1:10) to give the following products:

a) 3 mg (2%) of *trans*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]hexan-2-one **1d**, R_f 0.36.

b) 90 mg (56%) of recovered starting enone, R_f 0.29.

c) 12 mg of white solid, R_f 0.17, which after recrystallization from methyl *tert*-butyl ether gave 10 mg (6%) of pure *cis*-5-α-naphthyl-6-β-naphthylbicyclo[3.1.0]hexan-2-one **1c**, and mother liquor gave 2 mg of a mixture of this isomer and *cis*-5-β-naphthyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **1a** in ratio 2:5 (according to ^{1}H NMR analysis).

All the compounds were identified by comparison with known data (^{1}H NMR, m.p.).[1]

II. Solid State photochemistry of 2-Methyl-4,4-diphenylcyclohex-2-enone 2.

Exploratory Photolysis of **2** was performed as described above for the enone **1**. To prevent possible melting of this relatively low melting material (m.p. 117-118 °C) during the photolysis the ice-water cooling was employed. Reaction mixtures were analyzed by ^{1}H NMR and compared with previously published data.[2] The data are summarized in the following table:

Conversion	0.05	0.06	0.075	0.08	0.1	0.11	0.17	0.29	0.39	0.53
Ratio **2a** / **2b**	1.0:1.0	1.0:1.0	1.0:1.0	1.0:1.0	1.0:1.0	1.0:1.6	1.0:2.0	1.0:6.0	1.:15.0	1:18.0
Fraction of **2a**	0.025	0.03	0.038	0.04	0.05	0.04	0.06	0.04	0.02	0.03
Fraction of **2b**	0.025	0.03	0.038	0.04	0.05	0.07	0.11	0.25	0.37	0.5

Conversion	0.63	0.7	0.79	0.91	1.0
Ratio **2a** / **2b**	1:40.0	1:80.0	0:1.0	0:1.0	0:1.0
Fraction of **2a**	0.02	0.01	0	0	0
Fraction of **2b**	0.61	0.69	0.79	0.91	1.0

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[1] Zimmerman, H. E.; St.Clair, J. D. *J. Org. Chem.* **1989**, *54*, 2125-2137.

[2] Zimmerman, H. E.; Zhu, Z., *J. Am. Chem. Soc.* **1995**, *117*, 5245-5262.

III. Synthesis of 4-α-Naphthyl-4-phenylcyclohex-2-enone 3.

The synthesis of this compound was based on the procedures of Zimmerman et al.[3]

<u>α-Naphthylphenylketone.</u> A solution of 96.0 g (0.75 mol) of naphthalene in 150 ml of 1,2-dichloroethane was added dropwise to the stirred solution of 105.4 g (87.0 ml, 0.75 mol) of benzoyl chloride and 100 g (0.75 mol) of $AlCl_3$ in 150 ml of 1,2-dichloroethane at ice-bath temperature. After addition was complete the reaction mixture was stirred at this temperature for 5 h and then at the room temperature for 24 h. Then it was poured into ice, treated with small amount of concentrated HCl, washed with water and steam distilled to remove solvents and unreacted starting materials. The dark residue was dissolved in 600 ml of ether, washed with water and dried over Na_2SO_4. After concentration in vacuo the crude product was recrystallized twice from ethanol to give 100 g (57%) of yellowish crystals, m. p. 68-70 ^oC (lit.[4] m. p. 74-76 ^oC).

<u>1-α-Naphthyl-1-phenylethylene Oxide.</u> Trimethylsulfoxonium iodide for this reaction was prepared according to the known procedure[5]. To the solution of 25.0 g (0.11 mol) of trimethylsulfoxonium iodide in 240 ml of DMSO, 2.9 g (0.12 mol) of NaH (prepared from 4.8 g of 60% suspension in oil, washed with pentane and dried in a nitrogen atmosphere) was added in small portions at the room temperature. After all the NaH dissolved to give a clear reaction mixture, a solution of 23.2 g (0.10 mol) of α-naphthyl phenyl ketone in 75 ml of DMSO was added during 10 min. The resulting mixture was stirred at room temperature for 1 h and at 60-65 ^oC for 2 h. The hot reaction mixture was poured into ice and quickly extracted with 300 ml of Et_2O. The organic layer was washed with water (5 times) and dried over Na_2SO_4. After concentration in vacuo 23 g of the crude product as an yellow solid was obtained. This was used for the next step without further purification. ^1H NMR spectrum showed no starting material in this product. Data on analytical sample (recrystallized from *tert*-butyl methyl ether): m.p. 92-93 ^oC, yellowish prisms. ^1H NMR ($CDCl_3$): δ 8.00 (dm, J = 8.4 Hz, 1H), 7.88 (m, 2H), 7.67 (dd, $J_1 = 7.2$, $J_2 = 1.2$ Hz, 1H), 7.56 - 7.37 (m, 3H), 7.30 - 7.17 (m, 5H), 3.47 (d, J = 5.4 Hz, 1H), 3.62 (d, J = 5.4 Hz, 1H).

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[3] Zimmerman, H.E.; Rieke, R.D.; Scheffer, J.R. *J. Am. Chem. Soc.* **1967**, *89*, 2033.

[4] Campbell, N.; Easton, W.W. *J. Chem. Soc.* **1949**, 340.

[5] Kuhn, R.; Trischmann, H. *Liebigs Ann. Chem.* **1958**, *611*, 117.

2-α-Naphthyl-2-phenylethanal. A solution of 0.8 g of p-toluenesulfonic acid in 200 ml of benzene was refluxed with Dean - Stark adapter for 15 h under nitrogen. The solution of 23 g of crude 1-α-naphthyl-1-phenylethylene oxide in 50 ml of benzene was rapidly added to the refluxing solution and refluxed for 2 h. After cooling to room temperature the mixture was washed with aqueous solution of $NaHCO_3$, water and dried over Na_2SO_4. After concentration in vacuo a crude product (21.5 g) as a dark oil was obtained. This was distilled in vacuo to give 15.0 g (61% from starting ketone) of aldehyde as an yellowish oil, b.p. 155-160 ^oC / 0.025 mm Hg. ^1H NMR ($CDCl_3$): δ 10.08 (d, J = 1.8 Hz, 1H), 7.95 - 7.77 (m, 4H), 7.55 - 7.10 (m, 8H), 5.61 (d, J = 1.8 Hz, 1H).

4-α-Naphthyl-4-phenylcyclohex-2-enone. To a solution of 15.0 g (61 mmol) of 2-α-naphthyl-2-phenylethanal and 4.4 g (5.1 ml, 63 mmol) of methyl vinyl ketone in 300 ml of anhydrous ether at 0 ^oC was added via syringe 3 M solution of KOH in ethanol (3.4 ml, 10.2 mmol). The resulting mixture was stirred for 1.5 h at 0 ^oC and for 4 h at room temperature. Then the mixture was washed with 300 ml of 10% HCl, water, concentrated aqueous solution of $NaHCO_3$, water twice and dried over Na_2SO_4. The solvent was removed in vacuo to afford an yellow oil which was crystallized from ethanol. After additional slow recrystallization from ethanol 12.5 g (69%) of pure product as yellowish prism crystals was obtained, m.p. 155-157 ^oC. IR (film): 3054, 2945, 1662, 1597, 1507, 1447, 1395, 1281, 1249, 778, 701 cm^{-1}. UV (benzene): λ_{max} = 312 nm (ε = 74). ^1H NMR ($CDCl_3$): δ 7.90 - 7.81 (m, 2H), 7.72 (dd, J_1 = 8.4, J_2 = 1.0 Hz, 1H), 7.60 - 7.45 (m, 2H), 7.42 - 7.15 (m, 7H), 3.14 - 3.00 (m, 1H), 2.90 - 2.76 (m, 1H), 2.51 - 2.29 (m, 2H). X-ray analysis of this dimorph showed space group $P2_12_12_1$. Another dimorph with m.p. 145-146 ^oC corresponding to space group $P2_1/n$ was resulted from recrystallization from ether or *tert*-butyl methyl ether.

IV. Photochemistry of 4-α-naphthyl-4-phenylcyclohex-2-enone 3.

1. Direct Solution Photolysis. A solution of 500 mg of enone **3** in 500 ml of benzene was degassed with nitrogen for 1 h and photolyzed for 15 min by irradiation with a 400 W mercury lamp equipped with a 0.2 M $CuSO_4$ filter. After concentrating in vacuo the oily product was chromatographed on silica gel (column 50×2.5 cm, eluent hexane - ethyl acetate 10:1) to give the following products:

a) 30 mg (6%) of *trans*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3d**, R_f 0.30, recrystallized from *tert*-butyl methyl ether to give colorless prisms, m.p. 140 - 141 °C. ^{1}H NMR (C_6D_6): δ 8.24 - 8.04 (broad s, 1H), 7.72 - 7.64 (m, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.44 - 7.20 (m, 6H), 7.16 - 7.0 (m, 3H), 2.78 (d, J = 9.3 Hz, 1H), 2.44 (d, J = 9.3 Hz, 1H), 2.30 - 1.84 (m, 3H), 1.20 - 1.03 (m, 1H). MS (m/e): 298.1348 (calc. for $C_{22}H_{18}O$ 298.1358). The structure of this compound was proved by single crystal X-ray analysis.

b) 160 mg (32%) of *trans*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3b** as a colorless oil, R_f 0.23. ^{1}H NMR (C_6D_6): δ 8.07 (d, J = 9.1 Hz, 1H), 7.64 - 7.44 (m, 3H), 7.28 - 7.06 (m, 6H), 7.0 - 6.92 (m, 1H), 2.84 (d, J = 9.6 Hz, 1H), 2.67 (d, J = 9.6 Hz, 1H), 1.92 - 1.63 (m, 3H), 1.14 - 0.98 (m, 1H). The structure of this compound was proved by photochemical interconversion to the corresponding *cis*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3a**.

c) 10 mg (2%) of starting enone, R_f 0.19.

d) 170 mg of mixture of *cis*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3a** and *cis*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3c** in a ratio 20:1, R_f 0.15. Recrystallization of this mixture from *tert*-butyl methyl ether gave pure *cis*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3a**. Further crystallization of mother liquor gave separate crystals of **3a** and *cis*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3c** which were mechanically separated. This procedure afforded 150 mg (30%) of *cis*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3a** as colorless prism crystals, m.p. 113-115 °C, and 7 mg (1%) of *cis*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3c** as colorless prisms, m.p. 149-150 °C. Spectral data for **3a** were the following: ^{1}H NMR (C_6D_6): δ 7.99 (d, J = 8.4 Hz, 1H), 7.47 (dd, J_1 = 8.4, J_2 = 1.0 Hz, 1H), 7.33 (td, J_1 = 8.4, J_2 = 1.0 Hz, 2H), 7.19 (d, J = 7.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.5 Hz, 1H), 6.73 - 6.60 (m, 5H), 2.93 (d, J = 3.4 Hz, 1H), 2.80 (d, J = 3.4 Hz, 1H), 2.35 - 2.21 (m, 1H), 2.1 - 1.81 (m, 3H). MS (m/e): 298.1361 (calc. for $C_{22}H_{18}O$ 298.1358). The structure of this compound was determined by single crystal X-ray analysis. Spectral data for **3c** were the following: ^{1}H NMR (C_6D_6): 8.18 (d, J = 8.5 Hz, 0.25H), 7.85 (d, J = 8.5 Hz, 0.75H), 7.61 (d, J = 8.5 Hz, 0.25H), 7.48 - 7.36 (m, 2.25H), 7.32 - 6.98 (m, 1.5H), 6.91 - 6.75 (m, 1.5H), 6.69 - 6.52 (m, 5H), 6.42 (d, J = 7.2 Hz, 0.5H), 2.81 (d, J = 3.3 Hz, 0.25H), 2.64 (d, J = 3.3 Hz, 0.75H), 2.58 (d, J = 3.3 Hz, 0.75H), 2.43 (d, J = 3.3 Hz, 0.25 H), 2.34 - 2.22 (m, 0.75H), 2.20 - 2.04 (m, 0.25H), 2.04 - 1.92 (m, 2.25H), 1.84 - 1.74 (m, 0.75H). MS (m/e): 298.1365 (calc. for

$C_{22}H_{18}O$ 298.1358). The structure of this compound was determined by single crystal X-ray analysis.

2. Exploratory Photolysis. The space group $P2_12_12_1$ crystalline material was irradiated. This experiment was performed as described above. The data are summarized in the following table:

Conversion	0.08	0.1	0.12	0.16	0.21	0.26	0.28	0.30	0.33	0.35
Ratio of (**3a**+**3b**) to (**3c**+**3d**)	1:1	1:1	1:1	1:1	1:1	1:1	1.2:1	1.3:1	1.2:1	1.5:1
Ratio **3c** / **3d**	1:6	1:6	1:6	1:6	1:1	1:6	1:5.5	1:5	1:5	1:5
Ratio **3a** / **3b**	1:3	1:3	1:3	1:4	1:3	1:3	1:2.5	1:2	1:2	1:1.3
Fraction of (**3c**+**3d**)	0.04	0.05	0.06	0.08	0.11	0.13	0.15	0.17	0.18	0.21
Fraction of (**3a**+**3b**)	0.04	0.05	0.06	0.08	0.11	0.13	0.13	0.13	0.15	0.14

Conversion	0.38	0.39	0.44	0.46	0.47	0.54	0.59	0.61	0.66
Ratio of (**3a**+**3b**) to (**3c**+**3d**)	1.9:1	1.5:1	1.5:1	1.6:1	2.4:1	3.2:1	3.3:1	2.2:1	3.4:1
Ratio **3c** / **3d**	1:4	1:4	1:4	1:3.7	1:3.5	1:3.5	1:3.5	1:3.5	1:3.3
Ratio **3a** / **3b**	1:1	1:1	1:1	1:0.7	1:0.8	1:0.7	1:0.6	1:0.5	1:0.5
Fraction of (**3c**+**3d**)	0.25	0.21	0.26	0.28	0.33	0.41	0.45	0.42	0.51
Fraction of (**3a**+**3b**)	0.13	0.14	0.18	0.18	0.14	0.13	0.14	0.19	0.15

3. Preparative Solid State Photolysis. A 75 mg portion of enone **3** (dimorph with space group $P2_12_12_1$) was irradiated for 100 h under conditions described for enone **1** . The resulting mixture was separated by column chromatography (silica gel, column 35×1.5 cm, ethyl acetate - hexane 1:10) to give the following products:

a) 22 mg (29%) of *trans*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3d**, R_f 0.30.

b) 4 mg (5%) of *trans*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3b**, R_f 0.23.

c) 26 mg (35%) of recovered starting enone, R_f 0.19.

d) 13 mg (17%) of mixture of *cis*-5-phenyl-6-α-naphthylbicyclo[3.1.0]hexan-2-one **3a** and *cis*-5-α-naphthyl-6-phenylbicyclo[3.1.0]hexan-2-one **3d** in ratio 1.6:1 (according to ^{1}H NMR data), R_f 0.15.

All compounds had spectral data identical to known samples.

V. Crystallographic structural determination.

Each crystal was mounted on a glass fiber in random orientation. The intensities were collected on a Bruker-AXS P4 diffractometer with a Smart 1000 CCD area detector. The structures were solved by direct methods and refined in full-matrix least-squares with

SHELXTL.[6] H-Atoms were calculated at idealized positions and included in the structure factor calculation with fixed isotropic displacement parameters. The Crystallographic Information Files (cif-files) have been deposited at the Cambridge Crystallographic Data Center.

Table. Crystal data and data collection parameters

Data	**1**	**3**	**3**	**3a**	**3c**	**3d**
formula	$C_{26}H_{20}O$	$C_{22}H_{18}O$	$C_{22}H_{18}O$	$C_{22}H_{18}O$	$C_{22}H_{18}O$	$C_{22}H_{18}O$
formula weight (g/mol)	348.42	298.36	298.36	298.36	298.36	298.36
T [K]	133(2)	133(2)	133(2)	133(2)	133(2)	133(2)
crystal dimensions [mm]	0.24x0.20x 0.18	0.30x0.14x 0.10	0.46x0.40x 0.32	0.40x0.36x 0.14	0.25x0.18x 0.17	0.42x0.38x 0.08
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$C2/c$	Cc	$P2_1/n$
2θ range [^{o}]	$2<2\theta<28$	$2<2\theta<28$	$2<2\theta<28$	$2<2\theta<28$	$2<2\theta<28$	$2<2\theta<28$
a [Å]	19.563(39)	10.2365(19)	8.6684(11)	14.0404(14)	16.2811(12)	17.3187(15)
b [Å]	9.9861(15)	11.0129(19)	12.0613(12)	12.3301(10)	12.0907(9)	10.6686(11)
c [Å]	20.8531(40)	14.289(3)	15.2919(17)	19.1415(18)	10.2117(7)	17.6405(17)
α [deg]	90	90	90	90	90	90
β [deg]	114.809(3)	90	105.528(2)	105.950(2)	127.6350(10)	103.764(3)
γ [deg]	90	90	90	90	90	90
V [Å^3]	3698.3(12)	1610.8(5)	1540.4(3)	3186.2(5)	1591.9(2)	3165.8(5)
Z	8	4	4	8	4	8
ρ_{calc} [g/cm^3]	1.252	1.230		1.244	1.245	1.252
μ [mm^{-1}]	0.074	0.074	0.077	0.075	0.075	0.075
total reflections measured	8746	3624	3540	3722	3484	7392
independent reflections	2546	1924	2652	2311	2940	3332
No. of variables	578	208	208	208	208	415
criterion	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$	$I>2\sigma(I)$
final R [%]	7.87	5.01	4.44	5.11	4.35	5.6
$wR2$ [%]	17.56	9.31	11.10	11.77	10.90	11.82
goodness of fit	0.912	0.931	1.069	0.996	1.025	0.880

VI. General mathematical treatment.

Suppose we have a solid state reaction in which two products - **A** and **B** - form. Consider the plot of amount of product **A** vs. total conversion c, which is given by equation *1*.

$$c = A + B \qquad (1)$$

At any infinitely small portion of a curve of a plot of A vs. c (see Figure 1), the slope α of the curve is given by equation *2*:

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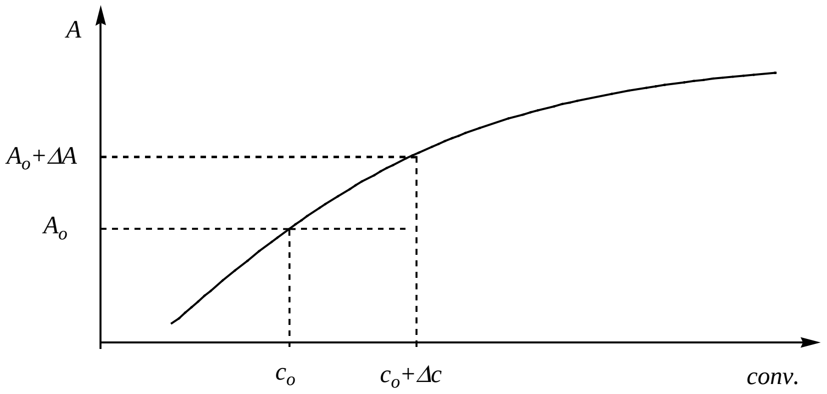
[6] SHELXTL™, version 5.1, 1997. Bruker AXS, Inc., Madison, Wisconsin, 53719, USA.

$$slope = \alpha = \Delta A / \Delta c = \Delta A / (\Delta A + \Delta B) \tag{2}$$

Figure 1.



Define R as ratio of two products at the conversion $c = c_0 + \Delta c$:

$$R = \frac{A_0 + \Delta A}{B_0 + \Delta B} \tag{3}$$

where A_0 is the amount of **A** at conversion c_0.

We obtain $R+1$ as follows:

$$R+1 = \frac{A_0 + \Delta A + B_0 + \Delta B}{B_0 + \Delta B} = \frac{c}{B_0 + \Delta B}$$

which gives:

$$\Delta B = \frac{c}{R+1} - B_0 \tag{4}$$

Analogously, the expression for $(R+1)/R$ is:

$$\frac{R+1}{R} = \frac{c}{A_0 + \Delta A}$$

which gives the equation for ΔA:

$$\Delta A = \frac{cR}{R+1} - A_0 \tag{5}$$

Combining together equations *2*, *4*, and *5* gives expression for slope:

$$\alpha = \frac{cR - A_0(R+1)}{(c - c_0)(R+1)} \tag{6}$$

where $c_0 = A_0 + B_0$.

Analogously, solving for B gives:

$$\beta = \frac{\Delta B}{\Delta c} = \frac{c - B_0(R+1)}{(c - c_0)(R+1)} \qquad (7)$$

Now from the equations *6* and *7* one can find ratio of two slopes:

$$\frac{\alpha}{\beta} = \frac{cR - A_0(R+1)}{c - B_0(R+1)} \qquad (8)$$

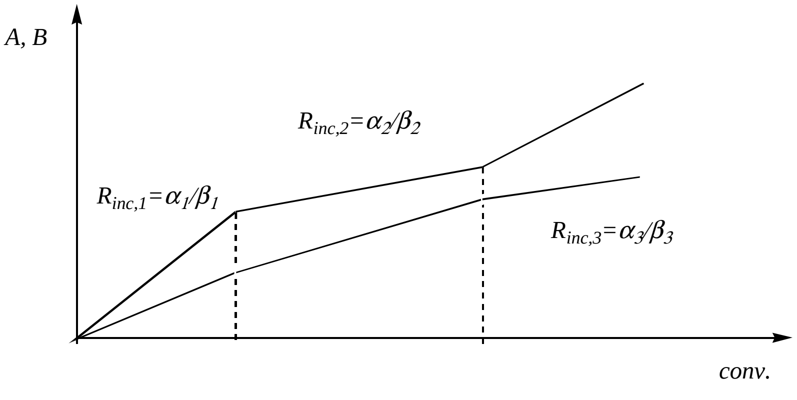
This equation exactly corresponds to the equation *1* in the paper. To get this general expression we did not use any limitations; hence it is valid for any case. Consider now the most important case of a stage process. If we are inside a definite stage (i.e. the ratio of product is constant inside this stage), the following equation is valid:

$$R = \frac{A_0}{B_0} = \frac{A_0 + \Delta A}{B_0 + \Delta B} \qquad (9)$$

In this case equation *8* becomes simplified:

$$\frac{\alpha}{\beta} = R_{inc} \qquad (10)\ [eq.\ 2]$$

Note, that here R_{inc} is an incremental ratio of products, and it is constant within any given stage. Thus we have a very simple way to treat a solid state stage reaction. One needs to get a plot of the amount (fraction) of each product vs. total conversion. Inside each stage the plot should be linear with the incremental ratio of product formation, R_{inc}, within each stage being equal to the ratio of slopes. This is general for the reactions with any number of products:



Related to this mathematical treatment is a matrix treatment. Consider now N experimental points A_n and N points B_n, corresponding to the fraction of products **A** and **B** at N experimental conversions C_n. R_n again is the ratio of the amount of product **A** to the amount of product **B**:

$$R_n = \frac{A_1 + A_2 + \ldots + A_n}{B_1 + B_2 + \ldots + B_n}$$

Using the approach similar that described above one can show for any point A_n the equation *11* is valid:

$$A_n = \frac{C_n R_n}{R_n + 1} - \frac{C_{n-1} R_{n-1}}{R_{n-1} + 1} \qquad (11)$$

For N points one can generalize equation 11 in matrix form:

$$\begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ \vdots \\ A_N \end{bmatrix} = \begin{bmatrix} \frac{1}{R_1 + 1} & 0 & 0 & \\ -\frac{1}{R_1 + 1} & \frac{1}{R_1 + 1} & 0 & \vdots \\ 0 & -\frac{1}{R_1 + 1} & \frac{1}{R_1 + 1} & \\ & \cdots\cdots & & \end{bmatrix} \begin{bmatrix} C_1 R_1 \\ C_2 R_2 \\ C_3 R_3 \\ \vdots \\ C_N R_N \end{bmatrix} \qquad (12)$$

Similarly, for the product **B** equation 13 is valid:

$$\begin{bmatrix} B_1 \\ B_2 \\ B_3 \\ \vdots \\ B_N \end{bmatrix} = \begin{bmatrix} \frac{1}{R_1 + 1} & 0 & 0 & \\ -\frac{1}{R_1 + 1} & \frac{1}{R_1 + 1} & 0 & \vdots \\ 0 & -\frac{1}{R_1 + 1} & \frac{1}{R_1 + 1} & \\ & \cdots\cdots & & \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \\ \vdots \\ C_N \end{bmatrix} \qquad (13)$$

Equations *12* and *13* can be rewritten in simple form:

$$\overline{\mathbf{A}} = \overline{\overline{\mathbf{R}}}\,\overline{\mathbf{C}_{\mathbf{R}}} \qquad (12a)$$

$$\overline{\mathbf{B}} = \overline{\overline{\mathbf{R}}}\,\overline{\mathbf{C}} \qquad (13a)$$

where the common multiplier $\overline{\overline{\mathbf{R}}}$ is a (N,N) matrix.