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# The Photochemistry of Racemic and Resolved 2-Iodooctane. The Effect of Solvent Polarity and Viscosity on the Chemistry.

by

Fang Gao, David Boyles, Rodney Sullivan,

Robert N. Compton, and Richard M. Pagni

## Supporting Material

**Analysis of Data from the Photolysis of *R*-2-Iodooctane.** The disappearance of the reactant was followed by gc/ms and corresponds to [R] + [S]. Because [R] + [S] = $[R]_0$ at t = 0, one can then obtain ([R] + [S])/$[R]_0$. For the changes in optical rotation the following equations are true.

$$f_R R_R + f_S R_S = R_{ob} \qquad (1)$$

$$f_R + f_S = 1 \qquad (2)$$

$$R_R = -R_S \qquad (3)$$

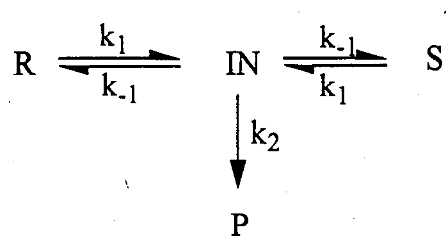
$$R_R = R_{ob} \text{ at } t = 0 \qquad (4)$$

where $f_R$ and $f_S$ are the mole fractions of the two enantiomers, $R_R$ and $R_S$ are the optical rotations of the two enantiomers, and $R_{ob}$ is the measured rotation. Substituting equations 2 and 3 into 1 yields

$$f_R = \frac{R_{ob} + R_R}{2R_R} \qquad (5)$$

From this and $f_S = 1-f_R$, one can easily calculate ([R] - [S])/$[R]_O$.

**Derivation of the Theoretical Equations for [R] + [S] and [R] - [S].** You are given the system



where R and S are the enantiomers of the substrate, IN is the intermediate (RP or IP), and P the products(s). If [R] = $[R]_O$ and [S] = 0 at t = 0, and F = $k_2/(k_2 + 2k_{-1})$, one derives the following equations if the steady state approximation is applied to IN

$$\frac{d([R]-[S])}{dt} = -k_1([R]-[S]) \tag{6}$$

$$\frac{d([R]+[S])}{dt} = -k_1F([R]+[S]) \tag{7}$$

Thus,

$$In\frac{[R]+[S]}{[R]_o} = -k_1Ft \quad \text{and} \tag{8}$$

$$In\frac{[R]-[S]}{[R]_O} = -k_1t \tag{9}$$

Suitable plots yield slopes whose ratio is F.

The Taylor series for $e^x$ where x = $-k_1Ft$ and $-k_1t$, respectively, are

$$e^{-k_1Ft} = 1 - k_1Ft + \frac{(-k_1Ft)^2}{2} + \frac{(-k_1Ft)^3}{6} + \cdots \tag{10}$$

$$e^{-k_1 t} = 1 - k_1 t + \frac{(-k_1 t)^2}{2} + \frac{(-k_1 t)^3}{6} + \cdots \qquad (11)$$

Therefore, $$\frac{[R]+[S]}{[R]_O} = 1 - k_1 F t \qquad \text{and} \qquad (12)$$

$$\frac{[R]-[S]}{[R]_O} = 1 - k_1 t \qquad (13)$$

if one ignores the square and higher order terms. This is valid where $k_1Ft$ and $k_1t$ are small. One will observe zero-order behavior at "short" times even for a first-order reaction.

The disappearance of R and S is genuinely zero order, the reaction scheme above will yield the following results.

$$[R] = [R]_O - k_1\left(\frac{1+F}{2}\right)t \qquad (14)$$

$$[P] = F k_1 t \qquad (15)$$

$$[S] = k_1\left(\frac{1-F}{2}\right)t \qquad (16)$$

Adding and substration equations 14 and 16 yields

$$[R] + [S] = R_O - Fk_1 t \tag{17}$$

$$[R] - [S] = R_O - k_1 t \tag{18}$$

Therefore,

$$\frac{[R] - [S]}{[R]_O} = 1 - \frac{Fk_1}{R_O} t \quad \text{and} \tag{19}$$

$$\frac{[R] + [S]}{[R]_O} = 1 - \frac{Fk_1}{R_O} t \tag{20}$$

The ratio of the slopes of equations 16 and 17 yields F.

Table. Photolysis of (*R*)-2-iodooctane. Disappearance of reactant and optical activity.[a]

| | cyclopentane | | | | | methanol | | | | | 2-methyl-2-propanol | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Reaction Time (hr) | $\frac{R-S}{R_O}$ | $\frac{R+S}{R_O}$ | $\frac{R}{R_O}$ | $\frac{S}{R_O}$ | ee | $\frac{R-S}{R_O}$ | $\frac{R+S}{R_O}$ | $\frac{R}{R_O}$ | $\frac{S}{R_O}$ | ee | $\frac{R-S}{R_O}$ | $\frac{R+S}{R_O}$ | $\frac{R}{R_O}$ | $\frac{S}{R_O}$ | ee |
| 0 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 0 | 1 |
| .25 | <.83 | >.83 | .83 | >0 | .99 | .75 | .97 | .86 | .11 | .77 | .86 | .94 | .90 | .04 | .91 |
| .50 | .74 | .76 | .75 | .01 | .97 | .63 | .83 | .73 | .10 | .76 | .74 | .80 | .77 | .03 | .93 |
| 1 | .57 | .69 | .63 | .06 | .83 | .35 | .71 | .53 | .18 | .49 | .50 | .63 | $.56_5$ | $.06_5$ | .79 |
| 1.5 | .39 | .61 | .50 | .11 | .64 | .10 | .50 | .30 | .20 | .20 | .31 | .57 | .44 | .13 | .54 |
| 2 | .13 | .55 | .34 | .21 | .24 | .03 | .31 | .17 | .14 | .10 | .15 | .31 | .23 | .08 | .48 |
| 3 | 0 | .52 | .26 | .26 | 0 | 0 | .20 | .13 | .13 | 0 | .05 | .06 | $.05_5$ | $.00_5$ | .09 |
| 4 | 0 | .50 | .25 | .25 | 0 | 0 | .12 | .06 | .06 | 0 | 0 | .03 | $.01_5$ | $.01_5$ | 0 |
| 5 | 0 | .46 | .23 | .23 | 0 | 0 | .08 | .04 | .04 | 0 | 0 | .01 | .01 | .01 | 0 |
| 6 | 0 | .40 | .20 | .20 | 0 | | | | | | | | | | |
| 9 | 0 | .28 | .14 | .14 | 0 | | | | | | | | | | |
| 12 | 0 | .22 | .11 | .11 | 0 | | | | | | | | | | |

(a) R and S represent the concentrations of the R and S enantiomers. $R_O$ is the concentration of the R enantiomer at t = 0. ee = % enantiomeric excess ÷ 100.