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## Type II Reaction of Organic Esters<sup>1,2</sup>

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**Abstract:** Organic esters, carbonates, and thiocarbonates all undergo type II elimination reactions. It is possible to determine the relative rate constants for competitive intramolecular hydrogen abstraction from the relative quantum yields of the type II olefins produced. The relative rate constants correlate with relative quantum yields because the experimental conditions are such that any intermediate (biradical) produced decomposes with unit probability to type II products. Treatment of the data for competitive type II reactions of these esters and data from the literature for dialkyl and aryl alkyl ketones using the equation  $\phi_1/\phi_2 = (AN_1/N_2) \exp(-\beta\Delta BDE/RT)$  reveals that all five series of compounds obey this relationship.  $A$  and  $\beta$  are constants derived from plotting the data according to eq II;  $\Delta BDE$  is the difference in the bond dissociation energies of the two  $\gamma$  C-H bonds involved in the two competing reactions. The factor  $N_1/N_2$  is the statistical ratio of the number of  $\gamma$  hydrogens available for each reaction. There are *no adjustable parameters* in this treatment.

Recent experiments have taken organic photochemistry out of the realm of a qualitative science and made quantitative understanding a reality. It has become possible to obtain quantitative information not only concerning the fate of excited molecules but also the factors which influence reactivity. Greatest progress has been made in the area of ketone photolysis, particularly with regard to the type II intramolecular hydrogen atom transfer reaction.<sup>4</sup>

The application of Stern-Volmer kinetics to the quenching of ketone excited states, in the liquid phase, has led to the determination of rate constants for hydrogen atom transfer in type II reactions. Electronic, steric, and solvent effects upon reactivity have also been identified. The most recent development has been the chemical detection of the biradical intermediate which heretofore had only been inferred.<sup>5</sup> It has long been known that the bond dissociation energy of the  $\gamma$  C-H bond was related to the efficiency of the type II reaction in ketones. Wagner's recent work has demonstrated that quantum yield for the type II process in aromatic

ketones does not correlate with the rate of hydrogen abstraction, because the biradical intermediate has a fairly high and variable probability of returning the hydrogen to the  $\gamma$ -carbon atom. Solvent effects are quite important in this connection.

It has been recognized that  $n-\pi^*$  excited states of ketones exhibit selectivity, in both inter- and intramolecular (type II) hydrogen atom abstraction reactions, which closely parallels the reactivity of alkoxy radicals. Previtali and Scaiano<sup>6,7</sup> have applied the bond energy-bond order method of Johnston and Parr<sup>8</sup> to calculate energies of activation and rate constants for the intermolecular abstraction of hydrogen by  $n-\pi^*$  triplets of organic carbonyl compounds. In order to compare their results with available data, most of which were for liquid phase systems, they assumed that the ratio of rate constants for two competing reactions is independent of phase and the preexponential factors are proportional to the number of hydrogens available for reaction. They arrived at the relationship

$$\frac{k_1}{k_2} = \frac{(\text{no H})_1 \exp(-E_{a1}/RT)}{(\text{no H})_2 \exp(-E_{a2}/RT)} \quad (\text{I})$$

which derives from the ratio of the Arrhenius equations for the two reactions.

(6) C. M. Previtali and J. C. Scaiano, *J. Chem. Soc. D*, 1298 (1971).

(7) C. M. Previtali and J. C. Scaiano, *J. Chem. Soc.*, 1667, 1672 (1972).

(8) H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, 85, 2544 (1963).

(1) (a) Supported in part by the National Science Foundation. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) Preliminary communications of part of this work: A. A. Scala and G. E. Hussey, *J. Org. Chem.*, 36, 598 (1971); A. A. Scala and J. P. Colangelo, *J. Chem. Soc. D*, 1425 (1971).

(3) Undergraduate research participant.

(4) For a review, see P. J. Wagner, *Accounts Chem. Res.*, 4, 168 (1971).

(5) P. J. Wagner and R. G. Zepp, *J. Amer. Chem. Soc.*, 94, 287 (1972).



**Table II.** The Competitive Type II Reactions of Carbonates

Compd	Temp, °K	Reaction 1 <sup>a</sup>			Reaction 2 <sup>a</sup>			R <sub>1</sub> N <sub>2</sub> /R <sub>2</sub> N <sub>1</sub>
		N <sub>1</sub>	Type γ H	Olefin (R <sub>1</sub> )	N <sub>2</sub>	Type γ H	Olefin (R <sub>2</sub> )	
Ethyl isopropyl carbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	6	1°	C <sub>3</sub> H <sub>6</sub>	0.178 ± 0.006
Ethyl propyl carbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	2	2°	C <sub>3</sub> H <sub>6</sub>	0.747 ± 0.013
	398	3	1°	C <sub>2</sub> H <sub>4</sub>	2	2°	C <sub>3</sub> H <sub>6</sub>	0.701 ± 0.029
Ethyl isobutyl carbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	0.50 ± 0.10
Methyl <i>sec</i> -butyl carbonate <sup>b</sup>	298	3	1°	1-C <sub>4</sub> H <sub>8</sub>	2	2°	2-C <sub>4</sub> H <sub>8</sub>	0.714 ± 0.007
Ethyl <i>tert</i> -butyl carbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	9	1°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	0.0426 ± 0.0036
<i>n</i> -Propyl isobutyl carbonate	298	2	2°	C <sub>3</sub> H <sub>6</sub>	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	1.02 ± 0.08
	398	2	2°	C <sub>3</sub> H <sub>6</sub>	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	1.06 ± 0.22
<i>n</i> -Propyl <i>n</i> -butyl carbonate	298	2	2°	C <sub>3</sub> H <sub>6</sub>	2	2°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	2.01 ± 0.05

<sup>a</sup> Both reactions 1 and 2 have O in the α position. <sup>b</sup> Olefins possible: 1-butene or 2-butene, from abstraction of a different γ hydrogen on the same side of the molecule.

**Table III.** The Competitive Type II Reactions of Thiocarbonates

Compd	Temp, °K	Reaction 1 <sup>a</sup>			Reaction 2 <sup>b</sup>			R <sub>1</sub> N <sub>2</sub> /R <sub>2</sub> N <sub>1</sub>
		N <sub>1</sub>	Type γ H	Olefin (R <sub>1</sub> )	N <sub>2</sub>	Type γ H	Olefin (R <sub>2</sub> )	
<i>S</i> -Ethyl isopropyl thiocarbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	6	1°	C <sub>3</sub> H <sub>6</sub>	0.50 ± 0.052
<i>S</i> -Ethyl propyl thiocarbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	2	2°	C <sub>3</sub> H <sub>6</sub>	0.35 ± 0.02
<i>S</i> -Ethyl isobutyl thiocarbonate	298	3	1°	C <sub>2</sub> H <sub>4</sub>	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	0.15 ± 0.006
	398	3	1°	C <sub>2</sub> H <sub>4</sub>	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	0.175 ± 0.001
<i>S</i> -Propyl ethyl thiocarbonate	298	2	2°	C <sub>3</sub> H <sub>6</sub>	3	1°	C <sub>2</sub> H <sub>4</sub>	2.08 ± 0.30
<i>S</i> -Isobutyl ethyl thiocarbonate	298	1	3°	<i>i</i> -C <sub>4</sub> H <sub>8</sub>	3	1°	C <sub>2</sub> H <sub>4</sub>	11.1 ± 0.63
<i>S</i> -Isobutyl <i>n</i> -propyl thiocarbonate	298	1	3°	<i>i</i> -C <sub>9</sub> H <sub>8</sub>	2	2°	C <sub>2</sub> H <sub>4</sub>	3.54 ± 0.16
<i>S</i> -Isopropyl ethyl thiocarbonate	298	6	1°	C <sub>3</sub> H <sub>6</sub>	3	1°	C <sub>2</sub> H <sub>4</sub>	1.0 ± 0.15

<sup>a</sup> Reaction 1 has S in the α position. <sup>b</sup> Reaction 2 has O in the α position.

pounds is the bond dissociation energy of the γ C–H bond. The importance of this factor in ester photolysis has been recognized before by Ausloos, *et al.*,<sup>11,12</sup> who observed a primary isotope effect in the photolysis of ethyl acetate-*d*<sub>4</sub> and also the preferential transfer of a secondary rather than a primary hydrogen atom in the photolysis of *sec*-butyl acetate and formate. Similar effects have also been recognized by Nichol and Calvert<sup>13</sup> and by Ausloos, *et al.*,<sup>12,14</sup> among others, in the type II reaction of ketones. These observations are to be expected if one makes the reasonable assumption that C–H bond breaking is occurring in the transition state.

During the course of our investigations we have found that the type II reaction occurs in each series of compound investigated and, because of the relatively large number of compounds studied, that the competitions are described by eq II, where  $\phi_1/\phi_2$  is the ratio

$$\phi_1/\phi_2 = (AN_1/N_2) \exp(-\beta\Delta BDE/RT) \quad (\text{II})$$

of olefins observed,  $N_1/N_2$  is the ratio of hydrogens available for each reaction, and  $\Delta BDE$  is the difference in the bond dissociation energies of the γ C–H bonds in reactions 1 and 2.<sup>15</sup>  $A$  is the ratio of the preexponential

factors for reactions 1 and 2 and  $\beta$  is a proportionality constant. It should be emphasized that there are *no adjustable parameters* in eq II. A plot of  $\ln(\phi_1 N_2 / \phi_2 N_1)$  against  $\Delta BDE/RT$  should be linear with a slope of  $\beta$  and an intercept of  $\ln A$ . Since  $\beta$  is the fractional contribution of bond energy to the activation energy, the limits of  $\beta$  are 0 and 1. The significance of  $A$  is uncertain. Although we have referred to  $A$  as the ratio of the preexponential factors, *i.e.*, an entropy term, a multitude of factors may determine the value of  $A$ . At this point it shall suffice to say that  $A$  represents the competition between reactions 1 and 2 when there is no difference in the γ C–H bond energy for these reactions.

The similarity of eq I and II is obvious. A treatment similar to that described has been applied in a limited way by Nichol and Calvert to the type II reactions of *n*-propyl alkyl ketones.<sup>13</sup> However, in their treatment the experimentally determined energy of activation difference was used in place of  $\beta\Delta BDE$  in eq II.

The somewhat surprising conformity of the data to eq II as indicated in Figures 1–3 prompted us to examine data from the literature on competitive type II reactions of dialkyl ketones in the gas phase. These data are presented in Table IV and plotted according to eq II in Figure 4. Again the agreement between the data and eq II is excellent. Although it is known that for aromatic ketones in the liquid phase quantum yields do not correlate with rate constants for hydrogen abstraction, sufficient rate constants are available to test the validity of eq II. These data which have been made relative to butyrophenone are given in Table V and plotted in Figure 5. Again the agreement is excellent.

Implicit in eq II are two assumptions which must be considered. The first of these is that the same excited state is being partitioned between two alternate paths,

(11) P. Ausloos and R. E. Rebert, *J. Phys. Chem.*, **67**, 163 (1963).

(12) R. P. Borkowski and P. Ausloos, *J. Amer. Chem. Soc.*, **83**, 1053 (1961).

(13) C. H. Nichol and J. G. Calvert, *J. Amer. Chem. Soc.*, **89**, 1790 (1967).

(14) P. Ausloos, *J. Phys. Chem.*, **65**, 1616 (1961).

(15) Since the γ-carbon atom is at least one methylene group removed from any atom other than carbon and hydrogen, we have assumed the bond dissociation energies of primary, secondary, and tertiary carbon hydrogen bonds to be the same as those values accepted for the appropriate alkanes. The values used are 98, 94, and 91 kcal/mol. These values are taken from (a) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965); (b) J. G. Calvert and J. N. Pitts Jr., "Photochemistry," Wiley, New York, N. Y., 1966. These same values have been used for each class of compound investigated.

Table IV. The Competitive Type II Reactions of Aliphatic Ketones

Compd	Temp, °K	Reaction 1			Reaction 2			$R_1N_2/R_2N_1$	Ref
		$N_1$	Type $\gamma$ H	Olefin ( $R_1$ )	$N_2$	Type $\gamma$ H	Olefin ( $R_2$ )		
4-Octanone	423	3	1°	$C_2H_4$	2	2°	$C_3H_6$	0.0939	13
	383							0.0795	13
	349							0.0550	13
4-Methyl-2-hexanone	423	3	1°	1- $C_4H_8$	2	2°	2- $C_4H_8$	0.0980	13
	357							0.0653	13
	317							0.102	13
2-Methyl-4-heptanone	423	3	1°	$C_2H_4$	6	1°	$C_3H_6$	0.730	13
	382	3	1°	$C_2H_4$	6	1°	$C_3H_6$	0.655	13
2-Pentanone-4,5,5- $d_3$	307	1	1°	$C_2HD_2$	2	1°	$C_2H_2D_2$	2.16	12
3-Methyl-4-heptanone <sup>a</sup>	423	3	1°	$C_2H_4$	3	1°	$C_2H_4$	1.00	13
4-Heptanone <sup>a</sup>	423	3	1°	$C_2H_4$	3	1°	$C_2H_4$	1.00	13

<sup>a</sup> Assumed equal participation by two equivalent sides of the molecule.

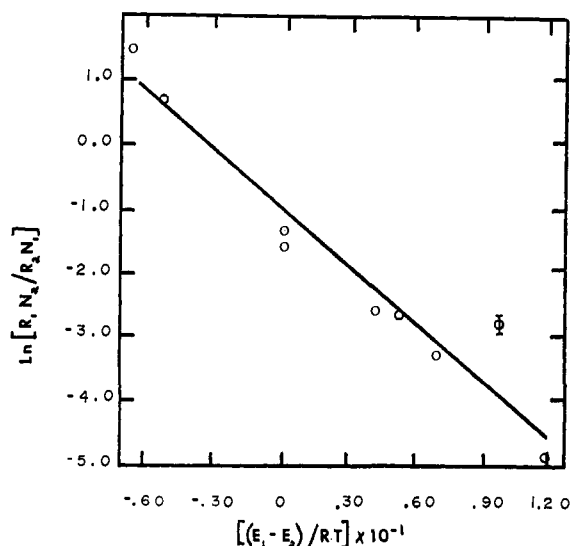


Figure 1. Ester photolyses. The dependence of the relative quantum yields of type II olefins upon differences in the  $\gamma$  C-H bond dissociation energies and temperature.

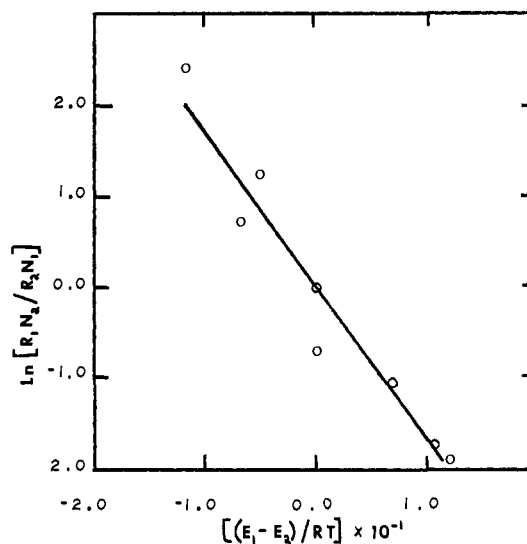


Figure 3. Thiocarbonate photolyses. The dependence of the relative quantum yields of type II olefins upon differences in the  $\gamma$  C-H bond dissociation energies and temperature.

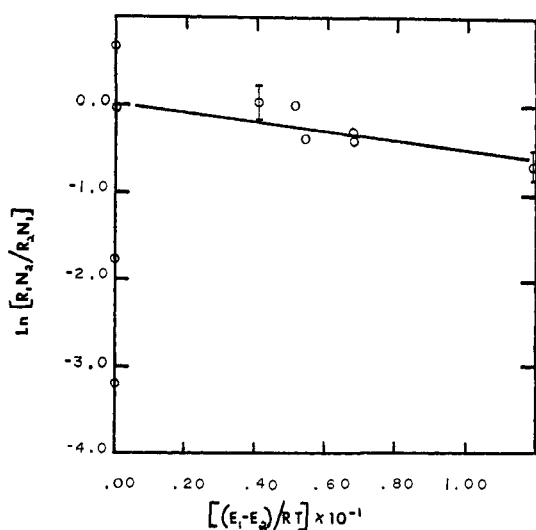


Figure 2. Carbonate photolyses. The dependence of the relative quantum yields of type II olefins upon differences in the  $\gamma$  C-H bond dissociation energies and temperature.

reactions 1 and 2. This is a reasonable assumption for the mercury-sensitized ester photolyses since the requirement of spin conservation and the existence of low-lying  $n-\pi^*$  excited states in each series of com-

Table V. The Competitive Type II Reactions of Aryl Alkyl Ketones<sup>a</sup>

Compd	$N$	Type $\gamma$ H	Olefin	$k_r \times 10^{-6}$	$k_r'N/k_rN'$ <sup>b</sup>
$\gamma$ -Methylvalerophenone	1	3°	$C_4H_8$	500	0.0044
<i>n</i> -Hexyl phenyl ketone	2	2°	$C_3H_{10}$	185	0.024
<i>n</i> -Heptyl phenyl ketone	2	2°	$C_6H_{12}$	185	0.024
<i>n</i> -Octyl phenyl ketone	2	2°	$C_7H_{14}$	161	0.027
<i>n</i> -Pentyl phenyl ketone	2	2°	$C_4H_8$	125	0.035
Valerophenone	2	2°	$C_3H_6$	116	0.038
$\beta$ -Methylbutyrophenone	6	1°	$C_3H_6$	20	0.66
Butyrophenone	3	1°	$C_2H_4$	6.6	1.00

<sup>a</sup> Temperature for all values 298°K. Reference 4. <sup>b</sup> Primed values designate butyrophenone.

pounds makes the  $n-\pi^*$  triplet the probable state involved. In most dialkyl ketones the  $n-\pi^*$  triplet is the predominant excited state for the type II reaction, and any type II reaction originating from the singlet state may in fact show selectivity similar to the triplet. The data for the aryl alkyl ketones are all for  $n-\pi^*$  triplet states and have been made relative to butyrophenone, since no intramolecular competition is possible for these compounds.

The second assumption in eq II is the use of quantum yields in place of rate constants. Wagner has demonstrated convincingly that, for aryl alkyl ketones in the

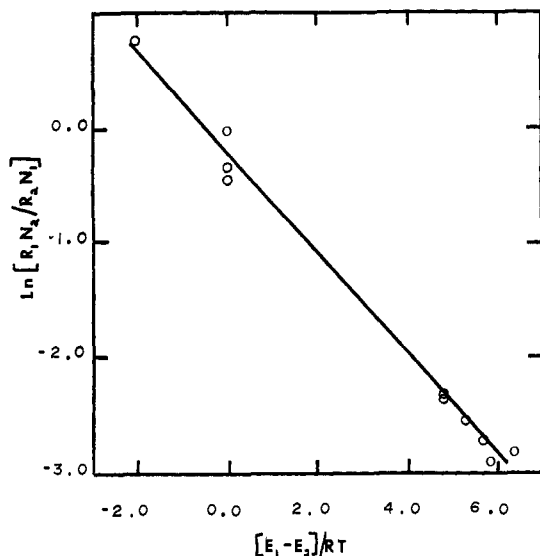


Figure 4. Dialkyl ketone photolyses. The dependence of the relative quantum yields of type II olefins upon differences in the  $\gamma$  C-H bond dissociation energies and temperature.

liquid phase, quantum yields do not correlate with excited state reactivity. The quantum yield for the type II reaction for these compounds is determined by three independent probabilities

$$\phi_{II} = \phi_e P_{BR} P_{II} \quad (III)$$

where  $\phi_{II}$  and  $\phi_e$  are the quantum yields for the type II reaction and the formation of the excited state leading to the type II reaction, respectively. The terms  $P_{BR}$  and  $P_{II}$  are the probabilities of forming the biradical intermediate from the excited state and the type II products from the biradical, respectively. These probabilities are given by eq IV and V. The terms  $k_r$  and

$$P_{BR} = k_r \tau_e \quad (IV)$$

$$P_{II} = k_{II} \tau_{BR} \quad (V)$$

$k_{II}$  are the rate constants for a hydrogen abstraction and collapse of the biradical intermediate to type II products, respectively. The lifetimes of the excited state and biradical are represented by  $\tau_e$  and  $\tau_{BR}$ , respectively. Combining equations III, IV, and V we arrive at eq VI which describes the dependence of the quantum

$$\frac{\phi_{II(1)}}{\phi_{II(2)}} = \frac{k_{r(1)}}{k_{r(2)}} \left[ \frac{k_{II(1)} \tau_{BR(1)}}{k_{II(2)} \tau_{BR(2)}} \right] \quad (VI)$$

yield ratio for two competing type II reactions upon the various rate constants involved.

Since the data for organic esters, carbonates, S-alkyl thiocarbonates, and dialkyl ketones do in fact obey the relationship in eq 2, we may ask how  $\phi_{II(1)}/\phi_{II(2)}$  could be a measure of  $k_{r(1)}/k_{r(2)}$  for these series of compounds. It would be an extremely unlikely coincidence for the term in brackets to have the same value for all of the compounds in a given series, except if  $\tau_{BR(1)}/\tau_{BR(2)} = k_{II(2)}/k_{II(1)}$  and the term in brackets reduces to one. The conclusion that  $\tau_{BR} = 1/k_{II}$  indicates that the only significant reaction of the biradical once it is formed is collapse to type II products. Thus the original expectation that a vibrationally excited biradical in the gas phase would preferentially decompose to type II products seems to have been real-

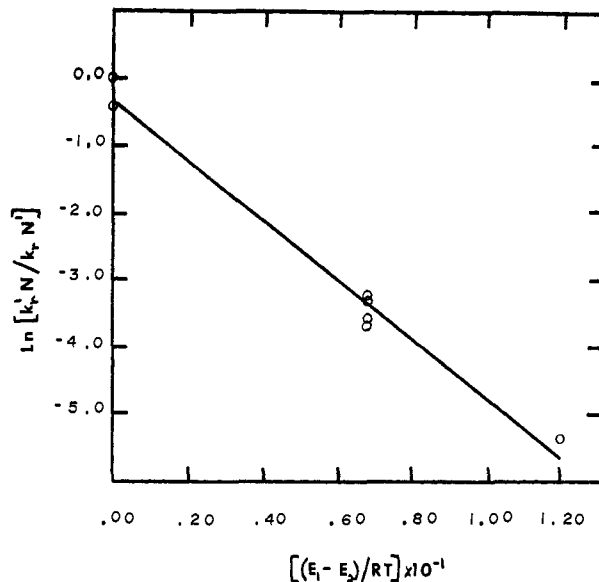


Figure 5. Aryl alkyl ketone photolyses. The dependence of the relative quantum yields of type II olefins upon differences in the  $\gamma$  C-H bond dissociation energies.

ized. Reversible hydrogen atom transfer does not occur in these gas phase systems.

A number of experiments have probed the question of reversible hydrogen atom transfer in esters and have not arrived at a satisfactory solution. Gano has examined this question in the liquid phase photolyses of *threo*- and *erythro*-1,2-dimethylbutyl acetates.<sup>16</sup> Using the relatively insensitive technique of nmr he concluded that reversible hydrogen atom transfer does not occur in these esters. On the other hand Pacifici and Hyatt have reported that the photolysis of neat (-)-2-methylbutyl benzoate resulted in a quantum yield for racemization of  $2.6 \times 10^{-3}$ . The details of this experiment have not been published.<sup>17</sup> The results of these liquid phase studies may have little bearing on the present gas phase studies.

We have examined this question by means of the technique used by Wagner to chemically detect the biradical in the liquid phase aryl alkyl ketone type II reaction.<sup>5</sup> After prolonged photolysis of isopropyl acetate in the presence of *i*-C<sub>3</sub>H<sub>7</sub>SD, no incorporation of deuterium into the ester was observed by mass spectrometry. On the other hand our gas phase photolysis of *erythro*- and *threo*-1,2-dimethylbutyl acetates resulted in the same *cis/trans* ratio for the type II olefin, 3-methyl-2-pentene. Therefore, it appears that an intermediate (biradical) is involved in the type II reaction of aliphatic esters. Its lifetime, however, is too short ( $\approx 10^{-10}$  sec) to permit chemical trapping or reverse hydrogen transfer to occur but long enough to permit rotation about the  $\beta$ - $\gamma$  carbon-carbon bond. This result is probably not surprising since the biradical which Wagner succeeded in trapping from the liquid phase photolysis of  $\gamma$ -methoxybutyrophenone was stabilized by hydrogen bonding to the solvent, delocalization of one radical center into an aromatic ring, and delocalization of the other radical center into an adjacent methoxyl group. All of these factors would increase the lifetime of the biradical and thereby make it more sus-

(16) J. Gano, *Tetrahedron Lett.*, 2549 (1969).

(17) J. G. Pacifici and J. A. Hyatt, *Mol. Photochem.*, 3, 271 (1971).

Table VI. Experimental Values of  $\beta$  and  $A$ 

Series	$\alpha$ position		Generic class	$\beta$	$A$	CC <sup>b</sup>
	X	Y				
I	CH <sub>2</sub>	O	Esters	0.30 ± 0.03 <sup>a</sup>	0.34 ± 0.007 <sup>a</sup>	0.965
II	O	O	Carbonates	0.05	1.04	
III	S	O	Thiocarbonates	0.17 ± 0.018	0.99 ± 0.14	0.969
IV	CH <sub>2</sub>	CH <sub>2</sub>	Dialkyl ketones	0.45 ± 0.015	0.84 ± 0.05	0.995
V	CH <sub>2</sub>	CH <sub>2</sub>	Aryl alkyl ketones	0.45 ± 0.027	0.72 ± 0.13	0.990

<sup>a</sup> Standard deviation. <sup>b</sup> Correlation coefficient.

ceptible to intermolecular trapping. Gano's liquid phase experiments of the same erythro and threo acetates led to the same conclusion as did the present experiment. However, some stereospecificity was observed in his direct photolysis experiments (singlet).<sup>16,18</sup>

The values of  $A$  and  $\beta$  derived from Figures 1-5 are presented in Table VI and require some consideration. The value of  $A$  is expected to be related to the relative entropy of activation for reactions 1 and 2 and should be strongly dependent upon the atom or group of atoms in the  $\alpha$  position. In cases where identical groups occupy the  $\alpha$  positions for reactions 1 and 2,  $A$  should be 1 and  $\ln A = 0$ . This can be seen to be approximately true for dialkyl and aryl alkyl ketones where CH<sub>2</sub> occupies the  $\alpha$  position. The line drawn in Figure 2 indicates this expectation even though the three experimental points having no bond dissociation energy difference do not lie on the origin. This will be discussed later. The values of  $A$  derived from Figures 1 and 3 where the atoms in the  $\alpha$  position are different are a measure of the extent of the competition between carbon and oxygen and sulfur and oxygen, respectively, when there is no bond dissociation energy difference between the  $\gamma$  C-H bonds. The data indicate that either oxygen or sulfur in the  $\alpha$  position leads to a more favorable transition state than an  $\alpha$ -methylene group.<sup>19</sup>

Equation II indicates an exponential dependence of the type II reaction upon  $\gamma$  C-H bond energies. This is reasonable if C-H bond breaking is occurring in the transition state. The value of  $\beta$  is a measure of the extent to which the C-H bond energy contributes to the energy of activation. Since in the transition state for the type II reaction at least one bond (O-H) is forming while the  $\gamma$  C-H is breaking, the bond dissociation energy of the bond broken will not contribute 100% to the energy of activation. The values of  $\beta$  which are determined from the slopes in Figures 1-5 are given in Table VI and are a measure of the extent to which the  $\gamma$  C-H bond energy contributes to the energy of activation. The larger the value of  $\beta$  for a particular series the more sensitive is the competition in these compounds to  $\gamma$  C-H bond energy differences. The value of  $\beta$  is actually determined by the slopes of the bond making and bond breaking potential energy surfaces.<sup>20</sup>

(18) The concept of spin correlation has recently been questioned: L. M. Stephenson and J. I. Brauman, *J. Amer. Chem. Soc.*, **93**, 1988 (1971).

(19) NEMO calculations by Dr. P. E. Stevenson of WPI indicate that the most favorable geometry for the cyclic transition state in the type II reaction is achieved when the  $\gamma$ -carbon atom lies out of the plane of the other atoms. Taking this into account the  $\gamma$ -hydrogen to carbonyl-oxygen distances are: CH<sub>2</sub>, 1.54 Å; S, 1.47 Å; O, 1.43 Å. The values of  $A$  may be a reflection of the ease with which the  $\gamma$ -hydrogen atom approaches the carbonyl oxygen.

(20) E. Warhurst, *Quart. Rev., Chem. Soc.*, **5**, 44 (1951).

The carbonates appear to obey the relationship except for the points which represent compounds with zero bond dissociation difference, *i.e.*, ethyl isopropyl carbonate, ethyl *tert*-butyl carbonate, and *n*-propyl *n*-butyl carbonate. Since the atoms in the  $\alpha$  position for reactions 1 and 2 are both oxygen, this leads to the expectation that  $A$  should be 1; the line in Figure 2 has disregarded these points and has been drawn through the origin. The slope of this line gives a value of  $\beta = 0.05$ , which indicates a relatively small dependence of the competition upon bond energy. We believe the separation of the three errant points from their expected position at the origin may be due to the extremely small dependence of the competition upon bond energy as indicated by  $\beta = 0.05$ . This relative insensitivity to bond energy differences may allow conformational effects which otherwise might be insignificant to become the dominant factors in the competitions. Consistent with this possibility is the parallel between the extent to which each point deviates from the origin and the expected magnitude of conformational effects. In the limit when  $\beta$  approaches zero there is no dependence upon bond dissociation energy and eq II becomes useless.

The present work confirms the occurrence of type II reactions in esters, carbonates, and thiocarbonates. It also demonstrates again the dependence of excited state reactivity upon the thermodynamic properties of coreactants. While qualitatively this is certainly to be expected, the quantitative nature of this dependence is surprising and worthy of further study.

### Experimental Section

All of the compounds used in this study were synthesized by the reaction of the appropriate acid chloride and alcohol. Purification was by repeated distillation on a spinning band column sometime followed by preparative gas chromatography. None of the compounds photolyzed was less than 99.0% pure and a few showed no impurities at all. The nmr spectrum of each ester was taken and was consistent with the structure.

Mercury-sensitized photolyses were conducted in cylindrical quartz cells, o.d. 45 mm, volume *ca.* 150 cm<sup>3</sup>, containing a drop of mercury. The light source was a Hanovia 87A-45 low-pressure mercury-vapor lamp. Since the envelope of the lamp is vycor, the radiation is pure 253.7 nm and contains none of the 184.9-nm mercury line. The pressure of the esters was their equilibrium vapor pressure at 25°. Although these were generally not measured they ranged from about 0.1 Torr for the higher molecular weight compounds to 2 Torr for the lower molecular weight compounds. In order to eliminate free radical products 5.0 Torr of nitric oxide was added before photolysis. The data given in the tables were determined at conversions of 0.5%. In all cases except the three high-temperature photolyses of esters (Table I),<sup>21</sup> saturated hydrocar-

(21) In the photolyses of esters (Table I) at elevated temperature an additional olefin was produced photochemically. This olefin apparently originated from the alkyl group attached to the carbonyl group. Isobutyl butyrate produced propylene while ethyl valerate and isobutyl valerate each produced 1-butene.

bons and olefins, other than those expected from the type II reactions, constituted less than 0.1% of the yield of the expected type II olefins. In cases where the photolyses were conducted in the absence of nitric oxide the major products observed were those expected from the free-radical reactions of the alkyl groups of the ester, with some contribution from smaller alkyl radicals. Products from the reactions of free radicals with nitric oxide did not undergo subsequent decomposition to produce olefins. Although a detailed study of the mechanisms of these free-radical reactions was not made, it could be estimated that the type II olefins accounted for approximately 1 to 10% of the hydrocarbon products. Hydrocarbon products were analyzed using a 30 ft, 0.25 in. o.d.

column packed with 20% squalane on 60-80 mesh Chromosorb P, operated at ambient temperature and a helium flow of 70 cm<sup>3</sup>/min.

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## Open Shell Interactions, Nonbonded Attraction, and Aromaticity. Implications for Regiochemistry

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**Abstract:** Molecules and transition state complexes can be constructed, in theory, from union of component fragments. Whenever one of these fragments has an open shell electronic configuration, there is a strong one-electron bias toward *cis* regioselectivity. This simple theoretical analysis can be used to rationalize unexpected chemical phenomena such as the greater stability of the *cis* relative to the *trans* isomer of various olefins, the *gauche* effect in conformational analysis, and the *cis* regioselectivity of cycloadditions.

Nonbonded interactions of substituents have been traditionally regarded as repulsive in nature<sup>1</sup> although a large body of experimental evidence seemed to indicate that in many instances such interactions can be attractive in nature. Some of this evidence is tabulated in Table I. In the last few years, some novel ideas regarding the nature of long range, or, nonbonded, interactions<sup>2</sup> have been discussed in the literature. Specifically, Woodward and Hoffmann<sup>3</sup> examined the effect of secondary attractive interactions on regioselection as part of their original formulation of the stereochemistry of pericyclic reactions. Hoffmann and Olofson<sup>4</sup> showed subsequently that nonbonded interactions which obtain in conjugated molecules and ions are important structural consequences, and Lowe<sup>5</sup> extended these ideas to problems in conformational analysis. Recently, Hoffmann<sup>6</sup> and his coworkers discussed the concept of steric attraction with particular reference to organic reactions and we showed that through bond and through space orbital interactions can lead to nonbonded attraction in various types of organic molecules and reactions.<sup>7</sup> In this paper, we have adopted a composite

molecule approach in order to elucidate the electronic factors which lead to nonbonded attraction in molecules and transition states. We consider the case of an open shell molecule or fragment<sup>8</sup> interacting with an open or closed shell molecule or fragment to form a product which arises from union of the two molecules or fragments. We shall examine the regioselectivity<sup>9</sup> of such processes and develop a general regioselection rule as a result of a simple theoretical analysis.

### Theory

We shall illustrate our approach by considering typical reactions of *cis*-difluoroethylene in its various open shell forms: (1) *cis*-difluoroethylene (CS) + excited *cis*-difluoroethylene (OS); (2) *cis*-difluoroethylene (CS) + *cis*-difluoroethylene cation radical (OS); (3) *cis*-difluoroethylene (CS) + *cis*-difluoroethylene anion radical (OS); (4) excited *cis*-difluoroethylene (OS) + *cis*-difluoroethylene cation radical (OS); (5) excited *cis*-difluoroethylene (OS) + *cis*-difluoroethylene anion radical (OS); (6) *cis*-difluoroethylene cation radical (OS) + *cis*-difluoroethylene cation radical (OS); (7) *cis*-difluoroethylene cation radical (OS) + *cis*-difluoroethylene anion radical (OS); (8) *cis*-difluoroethylene anion radical (OS) + *cis*-difluoroethylene anion radical (OS). Cases 1, 2, and 3 are typical reactions of a ground state, closed shell molecule and an open shell molecule, while cases 4, 5, 6, and 7 are typical reactions between two open shell molecules. The notation CS, in parentheses, stands for closed shell and the notation OS, also in parentheses, stands for open shell.

We first consider a typical closed shell-open shell case such as the reaction of excited *cis*-difluoroethylene and

(8) In a closed shell molecule all electrons are paired, while in an open shell molecule they are not.

(9) The term regioselectivity refers to the orientational preference in the union of two molecules.

(1) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956.

(2) The term nonbonded interaction usually denotes the combined internuclear and interelectronic interaction of two systems. In this paper, we are concerned with the interelectronic component of nonbonded interactions since the variation of the internuclear term is almost always intuitively obvious.

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(4) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

(5) J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970); J. P. Lowe, *Science*, **179**, 527 (1973).

(6) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Amer. Chem. Soc.*, **95**, 629 (1973).

(7) N. D. Epiotis and W. Cherry, *Chem. Commun.*, 278 (1973); N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 3087 (1973); N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Amer. Chem. Soc.*, **95**, 7558 (1973).