The depicted conformation of complex **12** is based on $^{19}F$ NMR studies performed on the ternary complex of FdUMP-5,10-methylenetetrahydrofolate-thymidylate synthetase in both the native[28] and denatured[28,29] states. These measurements of the C5-F analogue of **12** confirmed the fluorine atom to be in a pseudoequatorial position in the native enzyme complex, with C6-H also equatorial, and the Enz-S and C11-$CH_2$ bridge moieties in a trans-diaxial conformation.[28] Indirect measurement of $J_{HF}$ values between C5-F and C11-2H suggested that the C5-F bond (and therefore presumably the C5-H bond of the native species) was neither syn nor anti to the C11-N5 bond. Thus, whatever the conformation of the ternary complex, the enzyme must induce a conformation change prior to elimination.

The formation of the methyl group has been postulated to occur through the transfer of C6-H as a hydride equivalent to the exocyclic C5-methylene of the uracil ring mainly on the basis of model reactions.[30] This results in oxidation of the tetrahydropterin ring to the 7,8-dihydro form in a single two-electron step. However, tetrahydrofolate or tetrahydropterin oxidation by $O_2$, $Br_2$,[31] or ferricyanide[32] proceeds through a two-electron oxidation to quininoid dihydrofolate (or quininoid dihydropterin). The quininoid species then undergoes spontaneous rearrangement to the more stable 7,8-dihydro tautomer.[31] On chemical grounds the direct oxidation to 7,8-dihydrofolate necessitated by hydride transfer in the thymidylate synthetase reaction is less likely. Furthermore, Ehrenberg[33] has shown by electron spin resonance spectroscopy that a radical cation is formed in a chemical oxidation of tetrahydropterins, thus indicating that the two-electron oxidation to quininoid dihydropterin probably occurs in two one-electron steps.

These steps can then be extrapolated to the proposed mechanism for thymidylate synthetase shown in Figure 4. The placement of the two rings within **13** in a stacked conformation positions them for electron transfer. The first step in Figure 4 involves transfer of one electron from tetrahydrofolate to 5-methylene-dUMP to generate the radical cation **14** and the radical anion **15**. The enzyme could then rotate the methylene carbon directly under C6-H and facilitate abstraction of H· along a linear transition pathway. From this it is clear that attack of **11** must occur on the *si* face of **10** (i.e., the same side as C6-H). Transfer of H· from C6 of **14** to **15** then completes the reduction. Elimination of enzyme-SH finally gives (*S*)-methyl[7-$^1$H,$^2$H,$^3$H]-TMP (**16**) and 7,8-dihydrofolate.

Both the hydride and H· mechanisms are of course compatible with the stereochemical evidence.[34] It is our intent to suggest the possibility that quininoid species, which have been directly observed in hydroxylation reactions catalyzed by enzymes that require tetrahydrobiopterin,[16] may also be involved in one-carbon transfers involving tetrahydrofolate.

**Acknowledgment.** We thank Drs. Lloyd M. Jackman and Charles W. DeBrosse for their helpful suggestions and discussions and the National Institutes of Health for financial support (GM 24129).

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(34) Transfer of C6-H as a proton would require a prior two-electron reduction of 5-methylene-dUMP to generate a nonresonance stabilized carbanion at C7 of the incipient thymidine ring and is disfavored on those grounds.
(35) **Note Added in Proof**: The stereoselectivity of the chemical reduction may also stem from a stereoelectronic component with hydride approaching C11 antiperiplanar to the lone pair on N5, whose preferred orientation results from the favored cis ring junction in the product (Cieplak, A. S., personal communication).

# The Walling, El-Taliawi, and Zhao[1] "Carbonyl Effect" in Radical Brominations Is an Example of HBr Reversal. It Is Not Relevant to $\pi$ and $\sigma$ Radical Chemistry

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*Received July 27, 1983*

**Abstract:** Walling, El-Taliawi, and Zhao[1] claim that our "$S_\pi$ chemistry" is reproduced in photobrominations employing $Br_2$ in the presence of carbonyl compounds (no NBS). Photobromination of alkanes by *N*-bromosuccinimide (NBS) shows selectivities that vary, but which show limiting values for significant ranges of reaction conditions. We have attributed these different limiting values to three reaction paths which differ in involving either Br·, $S_\sigma$, or $S_\pi$ as the intermediate hydrogen-abstracting radical. Walling, El-Taliawi, and Zhao (WEZ) have reported selectivities they believe are attributable to a carbonyl-bromine intermediate rather than our $S_\pi$. Evidence is now presented to show that the WEZ results are due to HBr in varying amounts with *or without* carbonyl compounds present. This represents a fourth type of selectivity and one that is sensitive to HBr concentrations and probably arises in their systems from the following reaction: R + HBr $\rightleftarrows$ RH + Br·. There is no carbonyl effect. This fourth type had been deliberately excluded from our work, so that reactions involving HBr reversal are not relevant to our published work on succinimidyl chemistry. Thus, the selectivities (per H basis) for the neopentane/methylene chloride competitions stand without modification, as published earlier: 0.067, 1.0, and 17 for Br·, $S_\pi$, and $S_\sigma$, respectively.

Walling, El-Taliawi, and Zhao (WEZ) have stirred up a controversy[1] by challenging our hypothesis that both $\pi$ and $\sigma$ states are required to explain the thermal chain reactions of succinimidyl radicals generated in halogen abstraction reactions from *N*-bromo- or *N*-chlorosuccinimide.[2] The method of private approach having failed, it has been our reluctant duty to examine the evidence on which they based their claims. There are some areas of agreement.

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In the areas of disagreement, a number of their relevant experiments, on re-examination, were found to be flawed, leading to the rejection of most of their contradicting claims (details in an appendix to our most recent publication[3]). We address here the remaining major evidence and conclusion presented by WEZ, that brominations resembling those we attribute to the $\pi$ state are obtained with $Br_2$ in the presence of carbonyl compounds, such as trifluoroacetic anhydride, benzoic anhydride, succinimide, or *N*-phenylsuccinimide[1] [the WEZ "carbonyl effect"]. On this basis WEZ had concluded that "Skell's $S_\pi$ chemistry"[1] is better explained with a bromine atom complexed to the carbonyl compounds.[1]

Their argument does not bear directly on our $S_\pi$–$S_\sigma$ rationalization since we observed *the same $S_\pi$ behavior when bromine is removed with scavengers*,[2b,3] thus eliminating the possibility of a complexed bromine atom chain carrier. Nonetheless, we reexamined the experimental basis for the WEZ "carbonyl effect" to achieve a better understanding of their work.

When we repeat[4] the WEZ experiments, photoinitiated brominations ($O_2$ removed by vacuum degassing) of neopentane–methylene chloride mixtures, employing $Br_2$ in the presence of succinimide (and the HBr produced during the reaction), we obtain essentially the WEZ selectivity result, $r = 0.24$, a value WEZ claims is similar to the $r = 1.0$ we reported for $S_\pi$ ($r$ is the selectivity, calculated on a per hydrogen basis: $(k_+/k_{CH_2Cl_2})/6$). If the same experiment is carried out in the presence of suspended anhydrous potassium carbonate, an HBr scavenger,[5] we obtain $r = 0.067$. If anhydrous potassium carbonate and bromine (6:1 mole ratio) alone are used (no succinmide!), $r = 0.064$.[2] This is pure Br selectivity.[2,4] *Thus, there is no carbonyl effect if HBr is scavenged.*

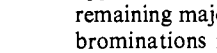
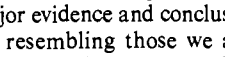
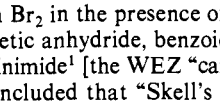
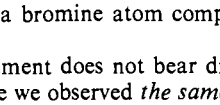
Precisely paired $Br_2$ brominations, of neopentane–methylene chloride mixtures, without control of [HBr] by scavenging, differing only by addition of succinimide (to 80% of saturation) to one of the reaction mixtures, gave selectivities of 0.39 *in the absence of succinimide*, and 0.31 in the presence of succinimide. In the presence of succinimide, $Br_2$, and HBr, a precipitate of the 1:1:1 adduct[6] develops during the reaction, accounting for the difference in values as a result of partial removal of HBr from the solution. *Thus there is no "carbonyl effect,"* only HBr reversal.

We cannot reproduce the WEZ claim that in the absence of succinimide the developing HBr alters the selectivities from an initial value of 0.057 to 0.027. This is especially puzzling since Walling also found that the same reaction mixture, if saturated with HBr at the start, yielded a much larger value of $r$.[7] It is our experience that selectivities obtained without HBr scavenging are variable, and the overall rates are much smaller than those obtained if HBr is scavenged by anhydrous $K_2CO_3$. We look forward to authoritative clarification of the effects caused by hydrogen bromide *from those who have been concerned with HBr-mediated reactions*, Walling, Tanner, Soumillion, Tedder, Zavitsas, and others. We have not intentionally worked in this area, and we have no plans to do so in the future.

We attribute the variable results of WEZ to a failure to remove the hydrogen bromide produced in the reactions. It is for precisely this reason that *all of our succinimidyl radical experiments had been carried out in the presence of an efficient hydrogen bromide scavenger*. It is a *non-relevant accident* that some WEZ values obtained without HBr scavenging approach the selectivity of 1.0 we report for $S_\pi$.

Our $S_\pi$ values are obtained either with HBr scavenging in the presence of $Br_2$ and NBS or by two other methods employing NBS, *with scavenging of both $Br_2$ and HBr*.[2d,3,4] The selectivities for neopentane/$CH_2Cl_2$ are as follows: Br, 0.067; $S_\pi$, 1.0; $S_\sigma$, 17.

Table I

| | $S_\sigma$ | $S_\pi$ | Br· |
|---|---|---|---|
| $r$(isobutane; 3°/1°) | 14 | 290 | 25,000 |
| $r$(butane; 2°/1°) | 3.5 | 12 | 750 |
| $r$(*neo*-$C_5H_{12}$/$CH_2Cl_2$) | 17 | 1.0 | 0.064 |
| $k_H/k_D$ ($CH_2Cl_2$/$CD_2Cl_2$) | 1.5 | 5.8 | 11.5 |
| $k_H/k_D$ ($CHCl_3$/$CDCl_3$) | 1.4 | 6.3 | 12.9 |
| $k$  $/k$  | 1.9 | 16.5 | large |
| S· + $C_6H_6$  | same rate as addition to alkenes | n.r. | – |
| S·  | major pathway | n.r. | – |

We conclude that since there is no carbonyl effect as claimed by WEZ, also this portion of their work does not present a challenge to our $S_\pi$–$S_\sigma$ hypothesis.

## Evidence for Two Succinimidyl Radicals

In response to a referee request we summarize here the salient experimental observations that have led us to the conclusion that two succinimidyl carriers are involved in these chain reactions.

In all instances the S· radicals are produced in halogen abstraction from NBS or NCS by a set of radicals in which the R–X produced cover a range of bond strengths, such that the $\Delta H$ of

$$NXS + R\cdot \rightarrow RX + S_\pi \text{ or } S_\sigma$$

the reactions producing the S· vary from 0 to −22 kcal/mol. The subsequent chemistries of the S· radicals fall into two categories defined by a dividing line of ~17 kcal/mol. More exothermic succinimidyl generating reactions all produce an identical $S_\sigma$; all less exothermic reactions produce the other, $S_\pi$, with properties not varying with the value of $\Delta H$ below the dividing line. The reaction selectivities of these succinimidyl radicals are contrasted with one another, and with the bromine atom chain carrier.

The $S_\sigma$ radicals are produced in the presence of alkenes which scavenge Br and $Br_2$. The $S_\pi$ are produced in three different systems: one in the presence of $Br_2$, which is useable only with substrates which do not react readily with Br·, and the other two in the presence of alkenes, in one system with $BrCCl_3$ as coreactant and in the other with benzene. Thus there are three highly diverse methods for generating $S_\pi$, either in the presence of $Br_2$ or with strict exclusion. In each of these systems HBr is scavenged by NBS.[6] With regard to the three $S_\pi$ methods, these markedly different systems show identical reaction selectivities with low reactivity substrates such as neopentane and methylene chloride; with high reactivity substrates, where a Br· chain carrier reacts rapidly, the $BrCCl_3$ and benzene methods only must be employed for studies of $S_\pi$ behavior.[2d,3]

Employing analogous methods the properties of two varieties of carboxy radicals,[8] $RCO_2$, have been examined, and two varieties of glutarimidyl radicals.[4] These systems differ from the succinimidyl in only one essential detail, the exothermicities of the borderline between the reactions generating the upper and the lower states. We believe the differing borderline energies reflect the different energy splittings of the respective $\pi$ and $\sigma$ states.

## Experimental[4]

**General.** $^1H$ NMR spectra were recorded on a Varian EM-360 spectrometer with chemical shifts reported on the $\delta$ scale relative to TMS. Gas chromatography analyses were carried out on either a Varian 1400 FID or HP5790 FID with a phenyl methyl silicone gum 1-$\mu$M-thick, 30-m × 0.311-mm column.

**Materials.** *N*-Bromosuccinimide obtained from Aldrich Chemical Co. was recrystallized from water. Succinimide obtained from Aldrich was recrystallized from ethanol. Methylene chloride was purified by successive extractions with concentrated $H_2SO_4$, distilled water, and 5% aqueous sodium bicarbonate solution and then dried with anhydrous

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calcium chloride and distilled from phosphorus pentoxide. Neopentane, Phillips 99%, was used without further purification. The bromine employed in this work was Mallinckrodt analyzed grade and was used without further purification. $K_2CO_3$ obtained from Fisher was ground to a powder and pumped on a vacuum line, with heating at 150 °C for 24 h prior to use.

**Photolysis Experiments.** All reactions were carried out in 30-mL-capacity Pyrex pressure tubes fitted with Teflon O-ring sealed needle valves. Reaction mixtures were degassed three times by a freeze-thaw technique, alternately freezing and evacuating (<0.1 $\mu$) at -196 °C and thawing to ambient temperatures. The sealed pressure tube was placed in a Pyrex water circulating bath maintained at 14-15 °C and irradiated with a 400-W medium-pressure mercury arc at a distance of 10 cm through two layers of Pyrex glass and 5 cm of water. Irradiation times of 1.0-2.5 h were employed, and reactants were stirred with a Teflon-covered magnetic stir bar. Absolute product analyses were obtained by gas chromatography, and if necessary by $^1$H NMR, employing internal standards in both cases. Products were identified by comparison of GC retention times and/or $^1$H NMR spectra of authentic samples. If gas chromatography was used the products were first washed with 5% aqueous sodium bisulfite and 5% aqueous sodium bicarbonate and dried with anhydrous $Na_2SO_4$.

**I. Bromine in the Presence of $K_2CO_3$.** (a) Bromine (0.80 mmol), $CH_2Cl_2$ (78.25 mmol), *neo*-$C_5H_{12}$ (3.50 mmol), and $K_2CO_3$ (4.95 mmol) were irradiated for 1.5 h; the reaction mixture is heterogeneous throughout. The color of the reaction mixture turned from red to orange. The product mixture was analyzed by GC: $CHBrCl_2$ (0.61 mmol), neo-$C_5H_{11}Br$ (0.011 mmol); $r$ = 0.067. (b) Bromine (1.20 mmol), $CH_2Cl_2$ (78.25 mmol), *neo*-$C_5H_{12}$ (3.50 mmol), and $K_2CO_3$ (7.40 mmol) were irradiated for 2.0 h. The reaction mixture remained heterogeneous throughout. The color change from red to orange. The product mixture was analyzed by GC: $CHBrCl_2$ (0.93 mmol), *neo*-$C_5H_{11}Br$ (0.0178 mmol); $r$ = 0.071. (c) Bromine (0.95 mmol), $CH_2Cl_2$ (78.25 mmol), *neo*-$C_5H_{12}$ (3.76 mmol), and $K_2CO_3$ (5.80 mmol) were irradiated for 2.0 h. The reaction mixture remained heterogeneous throughout. The color changed from red to orange. The product mixture was analyzed by GC: $CHBrCl_2$ (0.81 mmol), *neo*-$C_5H_{11}Br$ (0.015 mmol); $r$ = 0.064.

**II. Bromine in the Presence of Succinimide (the WEZ Experiment).** Succinimide (2.00 mmol), $CH_2Cl_2$ (24.5 mmol), *neo*-$C_5H_{12}$ (2.17 mmol), and bromine (1.00 mmol) were irradiated for 2.15 h. No color change was observed and the reaction mixture remained heterogeneous. The product was analyzed by GC: *neo*-$C_5H_{11}Br$ (0.0075 mmol), $CHBrCl_2$ (0.066 mmol); $r$ = 0.24.

**III. Bromine in the Presence of Succinimide and $K_2CO_3$.** Succinimide (2.00 mmol), $CH_2Cl_2$ (26.5 mmol), *neo*-$C_5H_{12}$ (1.65 mmol), $K_2CO_3$ (6.00 mmol), and bromine (1.00 mmol) were irradiated for 2.15 h. The reaction mixture remained heterogeneous throughout the irradiation period. The color change observed was red to a lighter shade of red. The product mixture was analyzed by GC: *neo*-$C_5H_{11}Br$ (0.0106 mmol), $CHBrCl_2$ (0.416 mmol); $r$ = 0.067.

**IV. Bromine with and without Succinimide; Paired Reactions. (a) Without Succinimide.** Bromine (1.95 mmol), $CH_2Cl_2$ (46.95 mmol), and *neo*-$C_5H_{12}$ (1.97 mmol) were irradiated for 1.25 h. The reaction mixture was homogeneous throughout the irradiation period. The product was analyzed by GC: *neo*-$C_5H_{11}Br$ (0.016 mmol), $CHBrCl_2$ (0.163 mmol); $r$ = 0.39. **(b) With Succinimide.** Bromine (1.95 mmol), succinimide (0.61 mmol), methylene chloride (46.95 mmol), and *neo*-$C_5H_{12}$ (3.27 mmol) were irradiated for 1.25 h. The initial reaction was homogenous and became heterogenous after ~45 min. The product was analyzed by GC: *neo*-$C_5H_{11}Br$ (0.013 mmol), $CHBrCl_2$ (0.10 mmol); $r$ = 0.31. Succinimide analysis by $^1$H NMR: 0.60 mmol, $\delta$ 2.65, $s$ 4 H.

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**Registry No.** NBS, 128-08-5; $H_2$, 1333-74-0; $D_2$, 7782-39-0; HBr, 10035-10-6; $C_6H_6$, 71-43-2; $CH_2Cl_2$, 75-09-2; $CHCl_3$, 67-66-3; *neo*-$C_5H_{12}$, 463-82-1; isobutane, 75-28-5; butane, 106-97-8; succinimidyl radical, 24344-83-0; butadiene, 106-99-0; 3,3-dimethyl-1-butene, 558-37-2.

# *Communications to the Editor*

## Biosynthesis of Vitamin $B_6$: Incorporation of a C-N Unit Derived from Glycine

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We have presented evidence for the occurrence, in *Escherichia coli* B mutant WG 2, which closely resembles the wild type, of two pathways to pyridoxol (**2**) (vitamin $B_6$), one major and one minor.[4] In the major pathway the entire carbon skeleton of pyridoxol is derived from glycerol in a specific manner:[5-7] five of its eight C atoms (C-2′, -3, -4′, -5′, -6) are derived from the primary carbon atoms of glycerol, the other three (C-2, -4, -5) from the secondary carbon atom of glycerol. On the basis of these findings, we proposed a chemically rational scheme for the major route to pyridoxol in *E. coli*, from three triose precursors.[5]

In the minor route, which can be conveniently studied in *E. coli* B mutant WG 3 in which the major route is blocked, the $C_3$ fragment of pyridoxal (**1**), C-5′, -5, -6, is not derived as a unit from glycerol. Two of it C atoms, C-5′ and C-5, are supplied by C-2 and C-1, respectively, of glycolaldehyde,[6] and preliminary evidence suggested that C-6 arises from a one-carbon unit which can, in turn, originate from C-2 of glycerol.[4]

We now present evidence that, in mutant WG 3, C-6 of pyridoxal is derived from C-2 of glycine. Carbon 2 of glycine does, indeed, originate from C-2 of glycerol[8] and also serves as a source of one-carbon units.[8] However, the incorporation of C-2 of glycine into pyridoxal does not take place via a one-carbon unit but by way of an intact glycine-derived C-N unit that gives rise to C-6, N-1 of pyridoxal.

In two separate tracer experiments (experiments 1 and 2), cultures of *E. coli* B WG 3 (1 L, 1.5 g/L glycerol, 50 mg/L glycolaldehyde)[9] were incubated in the presence of [2-$^{14}$C]glycine (250 $\mu$Ci, New England Nuclear). Pyridoxal (**1**) was isolated[10]

(1) Department of Chemistry.
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(12) Satisfactory spectral and analytical data were obtained for the new compound obtained in this reaction.

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