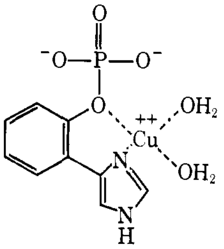
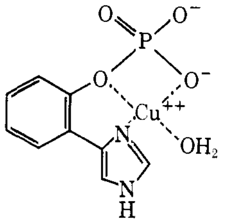
formation of additional higher order complexes in Cu^{2+}. These facts suggest that the transition state in the Cu(II)-promoted hydrolysis of I may be formulated as either **1** or **2**.



1



2

In **1**, the metal ion acts as a more effective acid catalyst than a proton, lowering the pK_a of the leaving group so that facile hydrolysis of the dianion—generally encountered only with leaving groups of pK_a < 7—may be observed. In **2** the Cu^{2+} may also serve to induce strain in the P–O bond and/or partially neutralize charge on the phosphate, leading to a nucleophilic displacement by solvent on phosphorus. It also is noted that hydrolysis of **2** *via* nucleophilic attack by water is kinetically indistinguishable from hydroxide attack on the monoanion of I. These second possibilities recall the rate accelerations of 10^5–10^7 encountered in strained five-membered cyclic phosphates and the 3200-fold enhancement in Cu^{2+}-catalyzed glycine ethyl ester hydrolysis, presumably owing to an increased susceptibility to nucleophilic attack as a result of chelation.

Solvolysis of I in mixed methanol–water solvents in the presence of Cu^{2+} displayed an identical methyl phosphate–inorganic phosphate product ratio with that observed in the uncatalyzed reaction, indicating no change of metaphosphate activity. This finding also rules against a possible phosphoramidate intermediate. If **2** or its kinetic equivalent represents the reaction pathway then one might have predicted a greater amount of methyl phosphate product owing to the more favorable susceptibility of **2** to nucleophilic attack on phosphorus. Further it might be expected that hydrolysis *via* **2** may proceed through preequilibrium formation of a pentacovalent phosphorus structure which would result in exchange between solvent and phosphoryl oxygens. When the hydrolysis of I in the presence of Cu^{2+} was conducted in H$_2{}^{18}$O-enriched water, no evidence of ^{18}O incorporation was observed. Thus it appears reasonable to argue that the Cu^{2+} ion in this reaction is acting simply as an acid catalyst. Analysis of the structure–reactivity relationship for phosphate esters[4] indicates that in order to account for the rate acceleration observed in this reaction, Cu^{2+} would have to lower the pK_a of the leaving group to p$K_a \approx 2$, a change of 6 pK_a units.

The results of this work indicate two important factors which should be considered in the design of future model systems: the requirement for a rigid structural geometry, and the binding of the metal ion to the alcohol leaving group. Compounds such as phenyl phosphate, which have no metal ion binding site other than the phosphate moiety, may show a retarded hydrolytic rate in the presence of metal ions; this is presumably due to binding of the phosphoryl oxygen, making metaphosphate expulsion less likely.

In compound I the juxtaposition of an excellent second binding site (imidazolyl nitrogen) promotes Cu^{2+} interaction with the ether rather than phosphoryl oxygens. The planar relationship between the chelating ligands, furthermore, favors formation of a typical Cu^{2+} square planar complex. The overall result is to confer hydrolytic ability on the normally nonreactive phosphate monoester dianion.

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Photolysis of Diazomethane in Tetrachloromethane. An Abstraction Reaction of Singlet Methylene

Sir:

In this communication we present evidence based on nuclear polarization studies that the singlet state of methylene is involved in *insertion* reactions into, and *abstraction* reactions from, tetrachloromethane.

Urry and Eiszner discovered the remarkable photoreaction of diazomethane in tetrachloromethane, which affords pentaerythrityl tetrachloride (**4**).[1a] This product arises from the reaction of one molecule of tetrachloromethane with four molecules of diazomethane, despite the large excess of tetrachloromethane. The high percentage yield of **4**, the high quantum yield of the consumption of diazomethane,[1b] and analogous reactions of diazomethane with other polyhalomethanes[1c,d] were accommodated in the free-radical chain mechanism outlined in Scheme I.[1b] The important features of this mechanism are (a) that photochemically generated methylene[2] abstracts a chlorine atom from the solvent to start the chain, (b) that intermediate α-chloro radicals, *i.e.*, A′, B′, and C′, are stable to the extent that they do not readily abstract chlorine atoms from the solvent, but still readily induce the decomposition of diazomethane (Scheme I, diagonal arrows), (c) that the intramolecular chlorine migration in β,γ-chloro radical intermediates A, B, and C (Scheme I, horizontal arrows) is considerably faster than any intermolecular reaction of these radicals, and (d) that D, an unstable primary radical without a chlorine atom in the β position, abstracts a chlorine atom from the abundant solvent. A more detailed insight into this reaction can be expected from utilizing the recent observation[5,6] that radical reactions may afford products with polarized nuclear spins (CIDNP effect), whose nmr spectra exhibit signals in emission (E) or enhanced absorption (A). This technique may allow one to detect products

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(1) (a) W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, 73, 2977 (1951); (b) W. H. Urry, J. R. Eiszner, and J. W. Wilt, *ibid.*, **79**, 918 (1957); (c) W. H. Urry and N. Bilow, *ibid.*, **86**, 1815 (1964); (d) N. Bilow, Ph.D. Dissertation, University of Chicago, 1956.

(2) Following a suggestion in the literature[3] the term "methylene" is employed to indicate that the divalent carbon intermediate, :CH$_2$, has a triplet ground state.[4]

(3) (a) R. M. Etter, H. S. Skovronek, and P. S. Skell, *J. Amer. Chem. Soc.*, **81**, 1008 (1959); (b) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *ibid.*, **84**, 4990 (1962).

(4) *Cf.* (a) R. A. Bernheim, W. H. Bernhard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970); (b) E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, **7**, 409 (1970).

(5) (a) J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch. A*, **22**, 1551 (1967); (b) J. Bargon and H. Fischer, *ibid.*, *A*, **22**, 1556 (1967).

(6) (a) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967); (b) R. G. Lawler, *ibid.*, **89**, 5519 (1967).

that are formed in minor amounts or are unstable under the conditions of reaction or work-up.

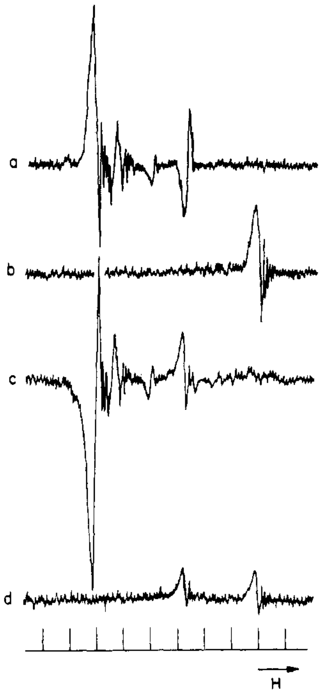
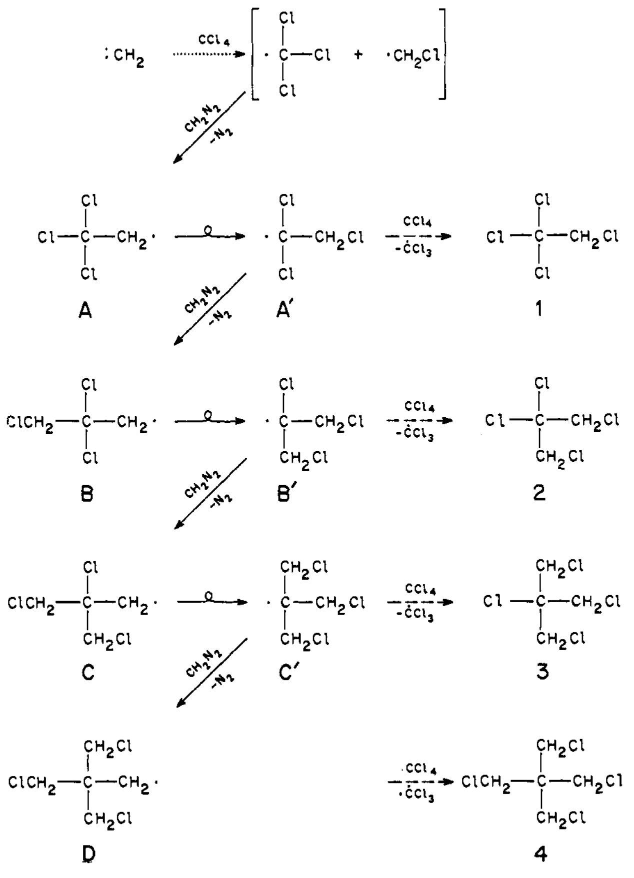


Figure 1. Fast-sweep 60-MHz spectra of solutions of diazomethane in carbon tetrachloride, before (b), during (a and c), and after ultraviolet irradiation. The solution used for recording trace (a) also contained 10% benzophenone. A frequency scale is given below trace d; the distance between two markers represents 10.6 Hz.

Scheme I



A dilute solution of diazomethane in tetrachloromethane, when irradiated in the cavity of an nmr spectrometer, exhibits four nmr signals (Figure 1c) which were identified by their chemical shifts as due to 1,1,1,2-tetrachloroethane (**1**, strong E), 1,2,2,3-tetrachloropropane (**2**, weak A), 1,2,3-trichloro-2-(chloromethyl)propane (**3**, very weak E), and **4** (weak A). Only the major product of this reaction, **4**, was formed in sufficient yield to allow its detection after the irradiation was discontinued (Figure 1d).[7]

An attractive mechanism for the formation of **1** is the recombination of a geminate radical pair, chloromethyl–trichloromethyl. The formation of this pair, and subsequent escape from its solvent cage, initiates the free-radical chain leading to **4**. It is only reasonable that some of these pairs recombine in their original cages (*two-step insertion*).

Our assignment of a spin multiplicity to the reactive intermediate, methylene, is based on the polarization of product **1**. Therefore, it is necessary to establish that the enhanced signal of **1** represents more than an insignificant percentage of that product. An approximate enhancement factor for **1** can be estimated crudely as follows. The signal of **1** is recorded in approximately ten times the starting intensity of the diazomethane signal when less than one-third of that material is decomposed. The yield of **1** is $<5\%$. Using these data one arrives at an enhancement factor of $\sim$600 ($10 \times 3 \times 20$). This value is large in comparison to most of the experimental values and comparable in magnitude to the ones predicted on the basis of theoretical considerations.[8] Therefore, the enhanced signal observed for **1** must represent a large percentage of that product.

Closs and Trifunac[12] have suggested that the spin multiplicity of a carbene which is involved in an abstraction reaction determines the spin multiplicity of the resulting radical pair, and thus the direction of the nuclear transitions in the product. In tetrachloroethane (**1**), the protons originating in the α position of the radical with lower g value[13] appear in emission. The accepted theory of magnetic polarization[9–11] can account for the according polarization only if the radical pair and consequently the methylene involved in its formation are of *singlet* spin multiplicity. For recombination from a triplet radical pair or for random recombination the signal of **1** is predicted to appear in enhanced absorption.[9–11]

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(7) It is noteworthy that the signal of diazomethane is considerably weakened during uv irradiation (Figure 1a and 1c) although the diazo compound is not completely decomposed, as documented by Figure 1d. Similar effects have been observed on various diazo compounds and azides upon uv irradiation in external magnetic fields of $<$1–16 kG. The nature of this phenomenon is currently under active investigation.

(8) Theoretical treatments of the phenomenon of CIDNP were carried out by Closs and coworkers,[9] Kaptein and Oosterhoff,[10] and Glarum.[11] Theoretical calculations of enhancement factors are included in these treatments.

(9) (a) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183, 2186, 7227 (1970); (b) G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970);

(10) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, 4, 195, 214 (1969).

(11) S. H. Glarum, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 040.

(12) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **91**, 4554 (1969).

(13) Trichloromethyl has a g value of 2.0091.[14] The g value of the chloromethyl radical is assumed to fall between the 2.0026 of the methyl radical[15] and the estimated 2.0080 of the dichloromethyl radical.[16]

(14) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).

(15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(16) M. Lehnig and H. Fischer, *Z. Naturforsch. A*, **25**, 1963 (1970).

Unambiguous evidence for the above assignment was obtained in the photosensitized decomposition of diazomethane. With benzophenone (10%) as sensitizer[17] the signal of **1** appeared in enhanced absorption (Figure 1a). This alteration of polarization[18] supports the evidence found in the direct photolysis, that the divalent carbon intermediate, methylene, is produced in the singlet state and that it reacts with the carbon–chlorine bonds of tetrachloromethane before intersystem crossing to the triplet ground state[4] can occur.

An important postulate is implicit in this conclusion. According to the theory of CIDNP,[9–11] any polarization of in-cage recombination products vanishes unless there is escape of radicals from their primary encounter cages. The free-radical chain reaction (Scheme I) demonstrates that some of the chloromethyl–trichloromethyl radical pairs separate, and the high quantum yield of this reaction indicates that a sizable fraction of these radicals initiate radical chains. Since it was shown above that the radical pairs are of singlet spin multiplicity, we conclude that *singlet methylene* is involved in the *abstraction* that initiates the chain reaction.

The results discussed above provide an interesting contrast to the mechanisms derived for the reaction of methylene with carbon–hydrogen bonds. The almost indiscriminate insertions into primary, secondary, and tertiary bonds in the liquid phase[19,20] were rationalized as "one-step-insertion" reactions of singlet methylene,[20,21] whereas the more selective "abstraction" reactions in the vapor phase were ascribed to the triplet spin multiplicity.[20,21] The mechanisms postulated for the reactions with the carbon–hydrogen and the carbon–chlorine bonds are *not* mutually exclusive, because the two types of bonds are considerably different.

A short comment on the enhanced signals of **2**, **3**, and **4** follows. The polarization of **2** and **3** is not altered upon the use of a triplet sensitizer, suggesting random recombination of radicals such as chloromethyl with trichloroethyl ($A' + \cdot CH_2Cl \rightarrow$ **2**) or trichloropropyl radicals ($B' + \cdot CH_2Cl \rightarrow$ **3**). This mechanism leads one to expect identical polarization for all four (six) protons of **2** (**3**) because two of them originate in the α position of one radical fragment ($\cdot CH_2Cl$) and the two (four) others in the β position of the other one (A′, B′). Making the reasonable assumption that A′ (B′) has a larger *g* value than the chloromethyl radical, one predicts enhanced absorption for both **2** (as is observed) and **3** (contrary to the experimental result). This discrepancy casts some doubt on the assumed mechanism.

The reaction mechanism leading to **4**, the unique eight-step sequence induced by a trichloromethyl radical, cannot explain any polarization of this product,[9–11] yet an enhanced signal is observed both upon direct irradiation (A), and when the triplet sensitizer is used (E). This result can be explained if **4** is formed *via* the competing reaction sequence

$$\mathbf{3} + :CH_2 \longrightarrow [C' + \cdot CH_2Cl] \longrightarrow \mathbf{4}$$

and $\cdot CH_2Cl$ (one α-Cl atom) has a larger *g* factor than C′ (three β-Cl atoms).

Alternatively, one can account for the high-field signals of Figure 1a and 1c by assigning them to small amounts of 1,2-dichloroethane, which has a chemical shift very close to that of **4**. The dichloroethane could be formed by reactions of chloromethyl radicals[22] which escape from their geminate counterradicals after a polarizing encounter. As mentioned above, such an escape is necessary if any polarization of in-cage products occurs.

At the present time, we are extending our studies to the generation of methylene and the chloromethyl radical from alternative sources and to the reactions of diazomethane with substrates such as **1**, **2**, and **3**.

Acknowledgments. We are grateful to Dr. Saul Meiboom and Mr. Richard Hewitt for their patient guidance during our use of a modified pmr spectrometer and we are indebted to Dr. Sivert H. Glarum for enlightening discussions.

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[17] The use of benzophenone as a triplet sensitizer in hydrocarbons is limited because it undergoes photoreductions *via* hydrogen abstraction.[9b] This problem does not exist in chlorinated solvents, because the oxygen–chlorine bond is not very attractive.

[18] A similar alteration of an enhanced signal upon triplet photosensitization was found in the decomposition of dibenzoyl peroxide: (a) A. M. Trozzolo, S. R. Fahrenholtz, and F. Heatley, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, No. ORGN 042; (b) R. Kaptein, J. A. Den Hollander, D. Antheunis, and L. J. Oosterhoff, *Chem. Commun.*, 1687 (1970); (c) S. R. Fahrenholtz and A. M. Trozzolo, *J. Amer. Chem. Soc.*, **93**, 251 (1971).

[19] W. v. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3225 (1956).

[20] D. B. Richardson, M. C. Simmons, and I. Dvoretzky, *ibid.*, **82**, 5001 (1960); **83**, 1934 (1961).

[21] *Cf.* H. M. Frey and R. Walsh, *J. Chem. Soc. A*, 2115, (1970), and references cited therein.

[22] Possible pathways to 1,2-dichloroethane include the induced decomposition of diazomethane (i) followed by radical transfer (ii). Step i should be diffusion controlled, whereas reaction ii should occur in the first few collisions of the 2-chloroethyl radical. Neither reaction i nor ii is acceptable as a polarization step.[9–11] However, it is reasonable that the polarization of chloromethyl radicals escaping from trichloromethyl–chloromethyl radical pairs is in part preserved through a diffusion-controlled reaction with a substrate of 0.1 *M* concentration.

$$\cdot CH_2\text{-}Cl + CH_2N_2 \longrightarrow \cdot CH_2\text{-}CH_2Cl + N_2 \qquad \text{(i)}$$

$$\cdot CH_2\text{-}CH_2\text{-}Cl + CCl_4 \longrightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + \cdot CCl_3 \qquad \text{(ii)}$$

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The Stereochemistry of Reactions Occurring at Iron–Carbon σ Bonds[1]

Sir:

An interest in the mechanisms of transformations involving carbon–transition metal σ bonds has led us to determine the stereochemistry of the reactions between *threo*-$(CH_3)_3CCHDCHDFe(CO)_2Cp$ (**1**) and molecular bromine, mercuric chloride, and sulfur dioxide, using an nmr procedure described previously.[2,3] This procedure depends on the fact that erythro and threo diastereomers of most substances having the composition $(CH_3)_3CCHDCHDX$ display distinct nmr spectra, reflecting preferred molecular conformations in which the bulky *tert*-butyl and X groups are trans

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[1] This work was supported by the National Science Foundation, Grant No. GP-14247, and by the National Institutes of Health, Grant No. GM 16020.

[2] G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

[3] R. J. Jablonski and E. I. Snyder, *Tetrahedron Lett.*, 1103 (1968); R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).